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The depositional and diagenetic history of the Westbury Formation (Upper Triassic) in South West Britain

The Depositional and Diagenetic History of the Westbury Formation (Upper Triassic) in South West Britain

By

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I confirm this is my own work and has not been submitted for any other degree with the exception of a University of Bristol PhD.

JHS. Macquaker.

20th. November 1987.

THE DEPOSITIONAL AND DIAGENETIC HISTORY OF THE WESTBURY FORMATION (UPPER TRIASSIC) IN SOUTH WEST BRITAIN.

A PhD. THESIS RESUBMITTED BY J.H.S. MACQUAKER, TO THE UNIVERSITY OF BRISTOL, NOVEMBER 1987.

Summary.

A detailed facies analysis of the Westbury Formation (Rhaetian, Upper Triassic) was undertaken in south west Britain on both outcrop and subcrop data, from sediments within two fault bounded basins:- The Worcester Graben and the Bristol Channel Trough.

Palaeogeographic reconstructions of the Upper Triassic suggest that south west Britain was covered by a shallow, marine, shelf sea which was cut off from the main part of Tethys to the south. Deposition in both the Bristol Channel Trough and the Worcester Graben was dominated by low energy processes, although periodic storms disrupted the water column and the sediment. The occurence of algae and the fact that storm waves were able to rework the sediment suggests that water depths were beneath fair weather wave base but not beneath storm wave base, i.e. within the photic zone in depths between 10m and 30m.

During the predominant low energy conditions, sapropelic muds were deposited. These muds are composed of:- fine detrital quartz, K feldspars, detrital illite and kaolinite and up to 10% authochtonous organic matter (the organic matter over the area has a variable provenance, but generally has a marine algal, dinoflagellate and bacterial signature). The presence of abundant organic matter suggests that the sediment and possibly the bottom were anoxic, which in this context was probably caused by high surface productivity and poor bottom water circulation. Anoxia excluded a macrobenthos but permitted an anaerobic microbial community to colonize the sediment. This community was dominated in the top few metres by sulphate reducers and in the deeper parts of the profile by methanogens. As a byproduct of their

metabolism the sulphate reducers catalysed the formation of authigenic pyrite, non-ferroan microsparry calcites and possibly authigenic phosphate, whilst the methanogens caused ferroan calcite cement precipitation.

Analysis of the organic matter from the two basins suggests that the degree of anoxia varied, with the Worcester Graben being more "anoxic" than the Bristol Channel Trough.

Intermittent storm events reworked the anoxic muds and carried into the basins arkosic/quartzitic sand and biogenic debris. They also created characteristic bedforms including:- guttercasts, collapsed ripples, end-on fabrics, graded rhythmites, conglomeratic units, symmetrical ripples and generally stired up the sediment. Further they caused the shells to disarticulate and be preserved predominantly convex-up. Storms also temporarily aerated the bottom waters allowing an opportunistic aerobic community to colonize the sediment and disrupting the anoxic bacterial profiles by producing aerobic/anaerobic interface environments. Aerobic respiration caused the pH to drop and some of the metastable carbonates and clays to dissolve; whilst the development of interface environments caused a sharp pH drop, where sulphide oxidation occured, and possibly glauconite and/or K feldspar formation (where K^+ ion activity was high). (As water depths were shallow phototrophic sulphide oxidation may have also occured).

With the return to low energy conditions, anoxia re-estabished itself in the storm units, consequently subsequent diagenetic processes were dominated by the effect of anaerobic organisms, in particular by sulphate reducers and methanogens. As before sulphate reducers catalysed the formation of pyrite and associated non-ferroan, bright luminescing sparry calcites and were probably indirectly associated with K feldspar precipitation, whilst the methanogens caused the precipitation of ferroan cements and possibly contributed to the high proportions of preserved phytane in some of the muds. Bacterially mediated oxygenation of the organic matter also caused an increase in the relative amounts of hopanoid compounds relative to the steroidal components.

The effects of deep burial diagenetic process are generally limited in the Westbury Formation. as indicated by:-

i) The organics which have high n-alkane odd over even preference indices (in the C-27 - C-35 n-alkane homologues), low temperature isomers in the steroidal and hopanoid fractions and the presence of unsaturated n-alkanes.

ii) The authigenic clays which are poorly crystalline and only have a random, "mixed-layer" illite/smectite phase.

Thus the shales in the study area have not been through the "oil generation window," although those in the Bristol Channel Trough are more mature than those in the Worcester Graben. However deeper processes (in particular dewatering) probably caused the development of the fibrous vein calcites and dissolution fabrics. Presumably as a consequence of, either thermal decarboxylation, or organic acid production processes.

Overall the Westbury Formation is a characteristic, epeiric sea sapropel, whose deposition was interupted by rare storm events. The storms briefly caused oxic deposition and introduced an exotic, detrital component. Dominant anoxic conditions meant that the organic matter preservation potential was high which allowed a diverse anaerobic microbial community to develop. This microbial community subsequently controlled most of the early diagenetic process i.e. carbonate mobilization, reprecipitation and neomorphism of the calcium carbonate and pyrite formation. Subsequent burial was not sufficient to cause significant modification of these features.

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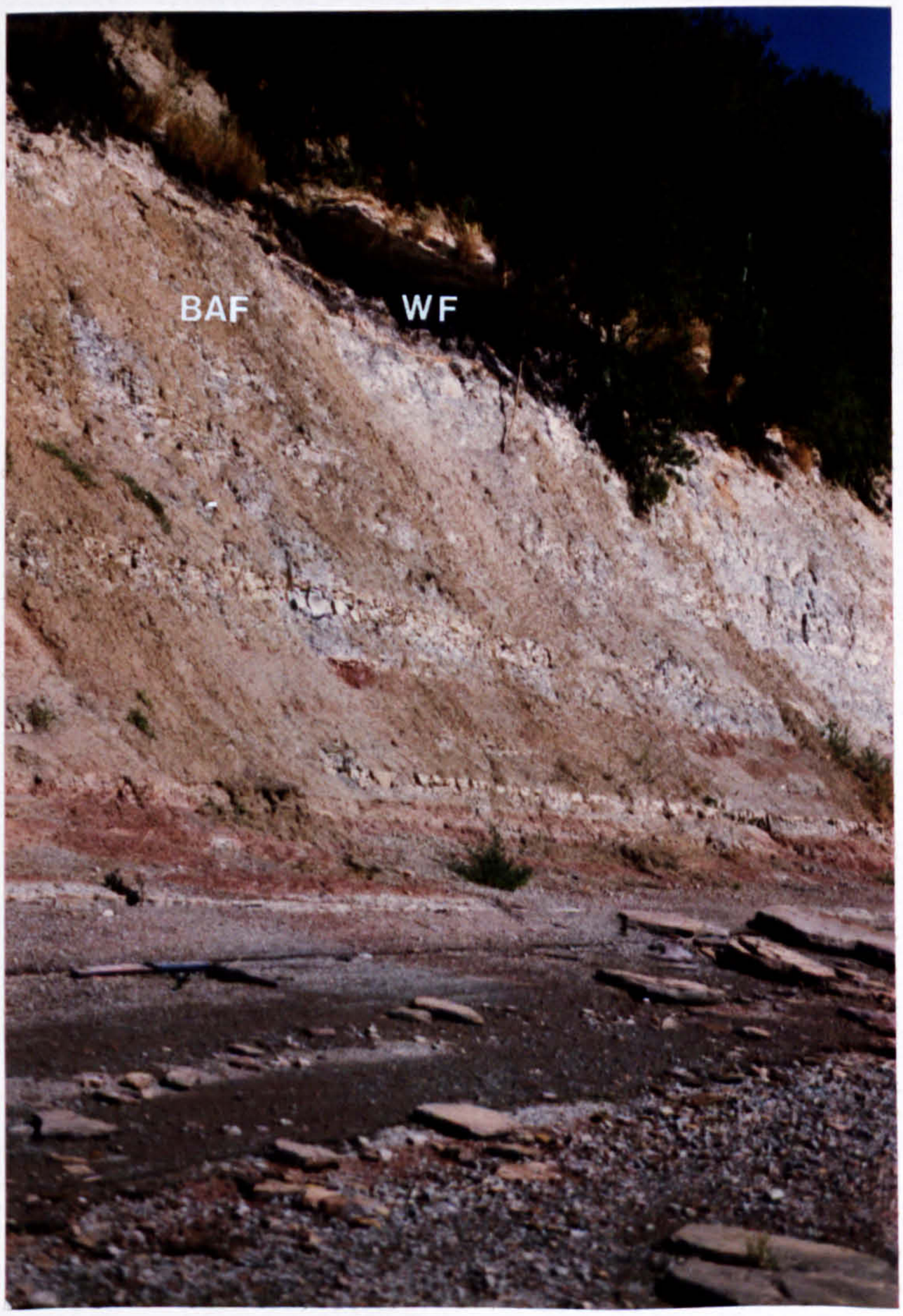
CHAPTER 1. INTRODUCTION

Section 1.1. Introduction and historical aspects of the study.

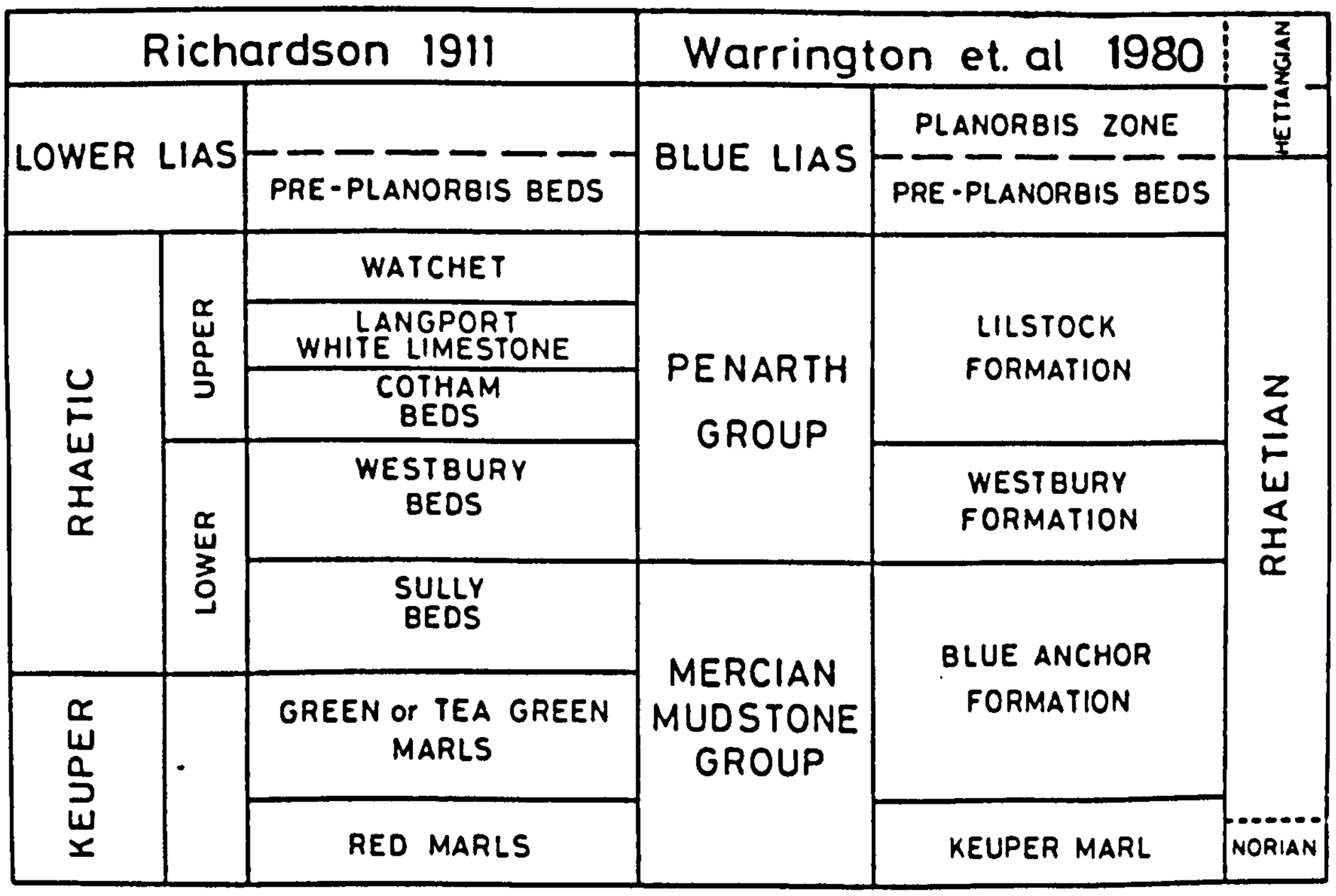
The depositional and diagenetic history of the Westbury Formation in the British Triassic is investigated in this work. The Westbury Formation is the basal lithostratigraphic unit of the Penarth Group and unconformably overlies the Blue Anchor Formation, which is the upper most unit of the Mercian Mudstone Group (plate 1.1).

Plate 1.1. The cliff section at Westbury-on-Severn, showing the Westbury Formation (WF) unconformably overlying the Blue Anchor Formation (BAF).



This unconformity extends regionally throughout Britain and broadly marks the end of Triassic continental deposition, and heralds the onset of "Jurassic" marine depositional conditions. The Upper Triassic lithostratigraphy is shown in figure 1.1, where the modern terminology (after Warrington *et al.* 1980) is compared with the earlier nomenclature of Richardson (Richardson 1911).

Figure 1.1. A comparison of the Upper Triassic stratigraphic nomenclature used by Richardson (1911) and Warrington *et al.* (1980).



After considerable debate by Richardson (1911), Arkell (1933), George *et al.* (1969), Audley-Charles (1970), Pearson (1970) and the reports of the Triassic and Jurassic Working Groups (Warrington *et al.* 1980 and Cope *et al.* 1980 respectively) the Westbury Formation is now placed by default within the basal part of the Rhaetian Stage, Upper Triassic, on account of the base of the Jurassic being defined on the first appearance of *Psiloceras planorbis*. In the United Kingdom the bivalve *Rhaetavicula contorta* and the dinoflagellate cyst *Rhaetogonyaulax rhaetica* are the zone fossils of the Rhaetian, as a consequence of the absence of *Choristoceras sp.* (plate 1.2) the characteristic zone fossil of similar age deposits in Europe.

Plate 1.2. *Choristoceras sp.* from Garmisch, Southern Germany.

Odin and Letolle (1981) and Armstrong (1982) have dated a number of Canadian lavas associated with the units containing *Choristoceras sp.* as being 204 ± 4 and 216 ± 4 million years respectively. Using these and other dates they argued that the Rhaetian was deposited over 7 ± 2 million years. Deposition of the Westbury Formation in Britain, in the context of this work, is thus assumed to have begun approximately 210 million years ago, and to have continued for approximately 2 million years (assuming that the Westbury Formation was deposited for 35% of the Rhaetian total).

Previous workers have concentrated on various specific aspects of the Westbury Formation. Early work dealt with palaeoenvironmental reconstruction (Moore 1861 and 1867), "bone-bed" deposition (Etheridge 1865, Davis 1881, Winwood 1881, Short 1904, Wickes 1904, Lloyd Morgan and Reynolds 1908, Richardson 1933 and Kellaway and Oakley 1934), stratigraphic

nomenclature (Opel 1858, Wright 1858 and Richardson 1911), documenting exposures (Richardson 1901, 1903, 1904, 1904, 1905, 1905, 1911 and 1933) and fossil description (Moore 1867). Whilst later research was concentrated on specific aspects of the sedimentology and palaeontology and the nature of limestone/shale cyclicity (Johnson 1950, Elliott 1953, Ivimey-Cook 1962 and 1974, Anderson 1964, Bazley 1968, Orbell 1973, Mayall 1979, Hamilton 1962 and 1977, Sykes 1977, Kelling and Moshriff 1977, Warrington 1976, 1977, 1978 and 1980, Antia 1979, Duffin 1980, Jones 1981 and Hallam and Shaarawy 1982). A brief historical rèsumè of the voluminous literature is presented in appendix 1.

Thus the established view of Westbury Formation deposition in south-west Britain is that it was laid down in restricted marine basins, which periodically developed bottom water anoxia: Consequently these basins only contained a restricted benthic fauna. The famous "bone-beds" were believed to have formed in response to winnowing on a migrating strand line associated with the Rhaetian transgression. Westbury Formation deposition is in marked contrast to the deposition of the marls and alternating marl/shales of the Mercian Mudstone Group and the finely laminated limestones of the Lilstock Formation, which are envisaged as having been deposited under hypersaline (Jeans 1978), lagoonal (Hamilton 1962 and 1977) and marginal marine conditions (Tucker 1977, Mayall 1979) with periods of emersion. Minor sea level variations during the deposition of the Westbury Formation are believed to account for the cyclic variations in the flora, fauna and sediment input, and to be the cause of the limestone/shale rhythms.

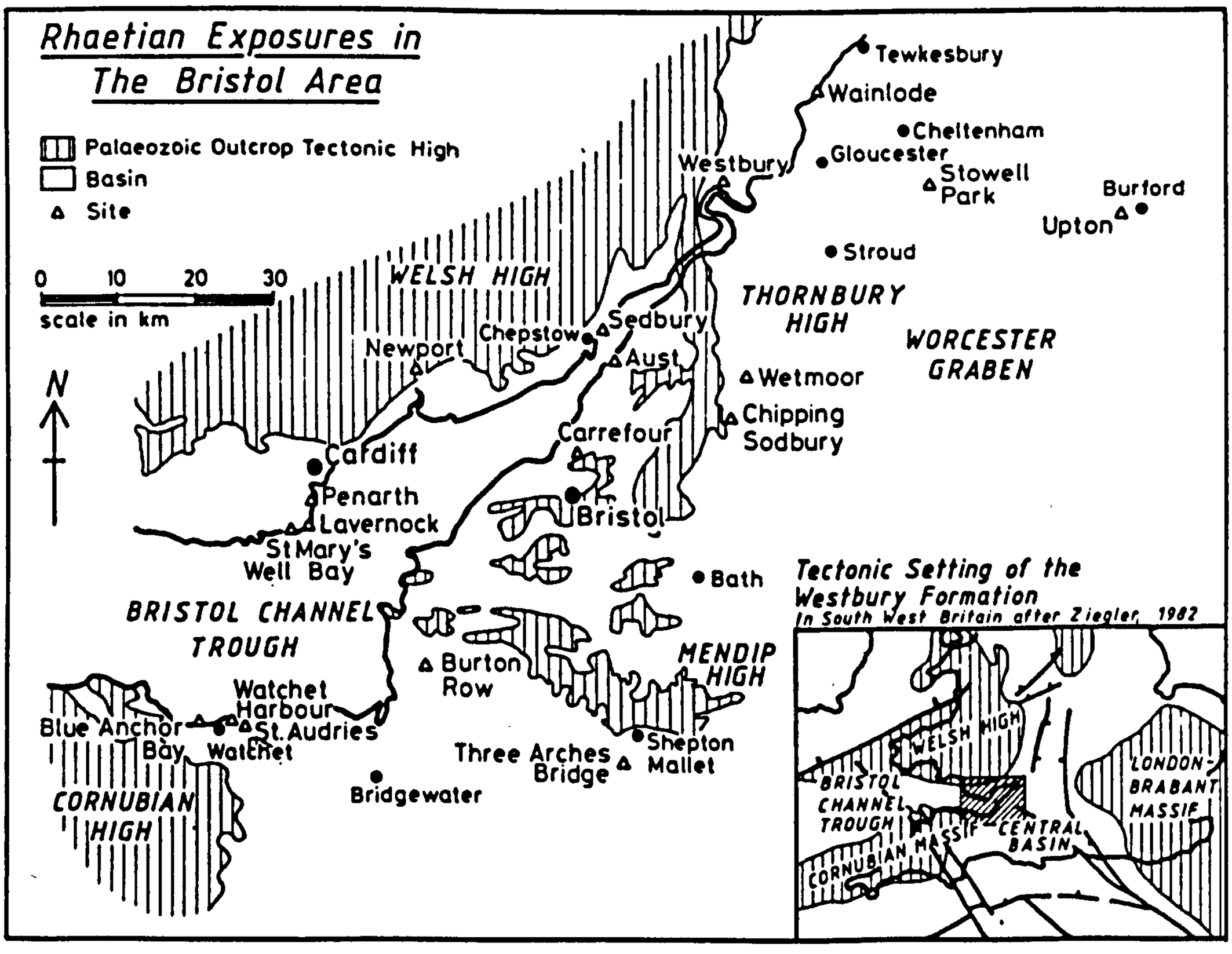
Section 1.2. Palaeogeographic and tectonic setting of the Upper Triassic in south-west Britain.

Upper Triassic facies in southern Britain and northern Europe were deposited under alternating lagoonal and restricted marine conditions at the north western end of Tethys (Sellwood 1978, Ziegler 1982). Restricted facies were deposited in this area because it was cut off from major Tethyan oceanic circulation patterns by extensive fringing reefs in southern Europe (Sellwood 1978).

During the deposition of Norian and Rhaetian facies in Europe, spatial and temporal fluctuations in salinity caused the interdigitation of marine (Alpine) and hypersaline (Germanic) facies (Jeans 1978). In Britain during the Norian hypersaline deposition predominated, while in the Rhaetian conditions were mainly marine. At the end of the Triassic, coupled with the Jurassic marine transgression, extensive marine facies belts developed across Europe; with carbonate banks forming in the south, (in northern Italy, southern France and southern Germany) (Zankl 1971, Fischer 1964, Flugel 1972 and Fabricus 1966) and interbedded organic rich shales and limestones in the north (in Britain, northern France and northern Germany).

In southern Britain deposition in the Upper Triassic and particularly in the Westbury Formation was influenced by three major graben systems; the northward trending Worcester Graben, the east/west trending Bristol Channel Trough and the Wessex Basin (see inset figure 1.2). These basins separate the "high" areas of the South Wales Massif, Mendips, London Brabant Platform and Cornubian Massif. It is not entirely clear if all or some of these tectonic "highs" were covered by water. Rhaetian vadose cave deposits are known from the Mendips, Thornbury High and South Wales High (e.g. Robinson 1957, Whiteside 1983) which indicates that island archipelagos were present at least on the northern boundary of the Bristol Channel Trough and Eastern boundary of the Worcester Graben, a point previously noted by Richardson (1901) (see figure 1.2).

Figure 1.2. A map of south-west England and Wales showing the field area and location of individual Westbury Formation exposures (open triangles). The map also shows the tectonic highs (hatched regions), which were probably land masses during the Upper Triassic (after Richardson 1911). The inset map shows the approximate position of the major basins that controlled sedimentation (unshaded regions) (after Ziegler 1982).



Westbury Formation deposition in south West Britain can thus be seen in context of deposition within small, restricted, marine basins cut off from the main oceanic circulation patterns of Tethys; in a climatic region hot enough to produce localized hypersaline conditions.

Section 1.3. Objectives of the investigation.

Previous research on the Upper Triassic of south west Britain has established a very uneven database for the Westbury Formation. Some workers - e.g. Sykes (1977), Duffin (1980), Bazley (1968), Ivimey-Cook (1962 and 1974) and Hallam and Sharaawy (1982) - worked extensively on the palaeontological aspects of the Westbury Formation. Others - e.g. Jones (1981), Mayall (1979), Antia (1979) and Kelling and Moshriff (1977) - concentrated on the sedimentological aspects of the unit and mainly on the arenaceous facies. Broadly all these authors proposed similar environmental models for the Westbury Formation, arguing that deposition occurred in nearshore brackish and restricted marine conditions, where variations in sea-level caused cyclic variations in the flora, fauna and rhythmic limestone/shale sedimentation.

Very little research has so far been directed at understanding Westbury Formation diagenesis, a process which is potentially significant as there was much organic matter (and hence a reducing agent) buried with the detritus.

This study therefore sets out to address a number of major and minor problems:

a.) To test the established models of Westbury Formation deposition (outlined in section 1.1), and in particular to assess the influence of sea-level changes on changing oxic/anoxic systems.

b.) To examine the shale units, particularly concentrating on the organic matter buried with the clay and mud fractions, to ascertain if the Westbury Formation is a good source rock for hydrocarbon exploitation and to determine where possible the provenance of the organic matter.

c.) To examine the diagenetic characteristics of the facies, and to assess if the limestone/shale cyclicity is a diagenetic or depositional phenomenon.

d.) To gain an insight into the geochemical conditions under which "bone-beds" form.

e.) To extend the seminal work of Jeans (1978) on the clays of the "Keuper Marl" (Mercian Mudstone Group) in order to determine if any unusual clay assemblages are present in the Westbury Formation, and if so do they reflect depositional or diagenetic variation?

f) To propose an intergrated model of Westbury Formation facies development, including both depositional and diagenetic features.

Section 1.4. General layout of the thesis.

The structure of this study is governed by classical techniques, so the initial chapter establishes the background to the work and defines the objectives of the investigation.

Chapter 2 outlines the rationale behind the sampling methodology and discusses in detail the three main laboratory based analytical procedures. It reviews the optical and electron optical microscopic techniques that were used, and includes discussions on: staining procedure, cathodoluminescence and electron optical analysis. It then deals with X-ray diffraction methodology, discussing both the analytical procedure and the interpretation of the data; and finally there is a review of gas chromatography and gas chromatography mass-spectrometry.

Chapter 3 initially describes the main facies types present in the Westbury Formation, and then reviews each facies in detail, discussing their specific depositional and diagenetic features and then proposes how each were formed.

Chapter 4 discusses the temporal and spatial relationship between the different facies types, and whether or not it is practical to correlate individual horizons across the study area.

Chapter 5 presents a general interpretation of the depositional and diagenetic mechanisms within the Westbury Formation. With particular emphasis on limestone/shale cyclicity, models of black shale deposition and black shale diagenetic mechanisms. The latter process is particularly discussed in terms of whether or not it is controlled by physiochemical or biochemical factors.

Chapter 6 concludes the study with a presentation of a unified facies model of the Westbury Formation, it discusses the limitations of this work and the implications that this work has for other limestone shale sequences.

Incidental data (notably the logs and organic geochemical data) are presented in appendices, with a brief historical resume of the voluminous Rhaetian literature, and a taxonomic discussion of the vertebrate and invertebrate faunas.

CHAPTER 2. METHODS.

Section 2.1. Field investigation and sampling methods.

After a literature search and preliminary reconnaissance, 16 localities were identified for a detailed facies analysis (listed in appendix 2) and a sampling programme was devised. Logs of each section were measured (appendix 3) and as far as possible unweathered samples from each lithology were collected, (unfortunately the latter was hampered by the deep weathering profile at many localities).

As shales are the dominant facies in the Westbury Formation, stratified sampling (after Flugel 1982), rather than interval collecting techniques were adopted. Stratified sampling involves collecting samples both vertically and laterally at every facies change and from each horizon. Further, in order to gain an insight into the variability within any one individual unit, where the shales exceeded 50 cm. and the limestones 5 cm. intermediate samples were taken at 25 cm. and 2.5 cm. intervals respectively. Overall approximately 275 sample stations and many more individual samples were examined (see appendix 3 for detailed sample locations).

A field, photographic record was maintained using Kodak, Kodacolor 100 and Kodak, Ektachrome 100.

Section 2.2. Optical mineralogical techniques.

(1) Thin section analysis.

Routine thin section analysis was performed on samples from the cemented units. The sections were ground to approximately 50 microns, and then stained with potassium ferricyanide and alizarin red S (Dickson *et al.* 1983). The staining was undertaken to reveal the distribution of different carbonate minerals (notably ferroan and non-ferroan calcite, ankerite, dolomite and siderite) and was designed to complement the luminescence study.

Selected, carbonate rich samples were also stained with titan yellow (after Choquette and Tausell 1978) to ascertain if there were any magnesium variations within the calcite. However in all cases stain uptake was uniform and apparently undifferentiated so the technique was abandoned.

Photomicrographs were recorded using Ektachrome 50 (tungsten balanced) film, and Kodacolor 100 (daylight balanced) film.

(2) Cathodoluminescence.

Cathodoluminescence techniques, henceforth abbreviated to CL. are becoming widely established in geology as a powerful tool in the analysis of diagenetic fabrics, particularly in carbonates.

Sample preparation for luminescence requires semi-polished specimens, and in this study polished thin sections were prepared using Hyprex 3 and 1 micron diamond lapping paste on a Engis, Kent 3 automatic lap. All the sections which had previously been stained were polished and re-examined using CL.

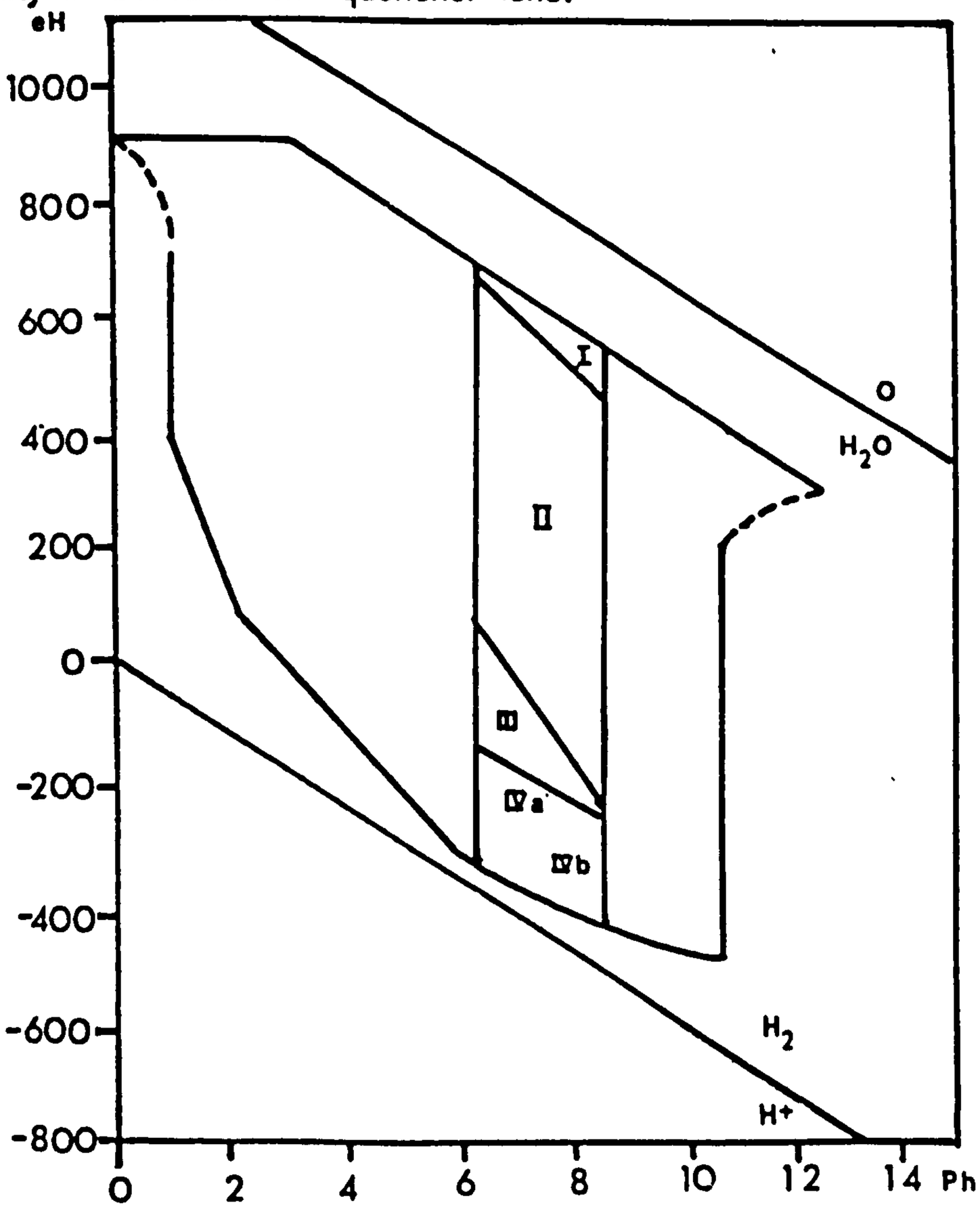
A comparison of two commercial and one home made luminoscope was undertaken, including a Nuclide belonging to the Department of Earth Sciences at the Open University, a Technosyn 8200, belonging to the Department of Geology at the University of Sheffield and a "home made" system belonging to Dr. J.A.D. Dickson of Cambridge University. All the systems were found to give similar results, although samples analysed in Dr. Dickson's system tended to have brighter luminescence characteristics. The operating conditions of the Nuclide were approximately standardized to 100 mTorr. at 14 Kv. and those of the Technosyn to 100 mTorr. at 16 Kv. Photomicrographs were recorded on Ektachrome 64 daylight film and Kodacolor 100 daylight film.

It is not the intention of this study to review the methodology and scope of CL. in detail, for such discussions the interested reader is directed to Nickel (1978), Sommer (1972), Meyers (1974) Grover and Read (1983),

Walkden and Berry (1984) and Fairchild (1983). Broadly however luminescence under electron bombardment is caused by lattice defects in the crystals (Nickel 1978), which in a geological context usually results from the presence of ion impurities. In carbonates and phosphates trace amounts of manganese are believed to cause luminescence (being the activator ion), whilst reduced iron is believed to quench luminescence. In feldspars the activator ion is probably titanium, although it is worth noting that feldspars have an intrinsic dull luminescence characteristic. As a result calcites that are activator ion rich and quencher ion deficient will tend to luminesce orange, dolomites red, phosphates a dull brown/yellow and potassium feldspars blue. Very low concentrations of manganese are known to cause luminescence in carbonates; for instance Ten Have (1983) has shown that concentrations as low as 15 p.p.m. will cause luminescence, whilst Fairchild (1983) found that concentrations of iron above 200-300 p.p.m. will quench luminescence, regardless of the amount of manganese.

CL. analysis often reveals complex light/dark zones within individual crystals. This zonation is believed to reflect subtle variations in the pore water redox potential associated with the growing crystal. Changes in redox potentials control the solubility of manganese and iron and thus their availability for incorporation into the calcite lattice. With this in mind Carpenter and Oglesby (1976) suggested that luminescence zonation may be used to chart the evolving pore water chemistry in diagenetic systems. They examined published data (Garrels and Christ 1965) on ion activity coefficients and mineral stabilities in different Eh/pH pore water environments and proposed that 5 luminescent zones were recognisable, with each zone corresponding to a unique field on an Eh/pH diagram (figure 2.1). They noted that each field would also have a characteristic stable mineral assemblage and thus they argued that by recognising the different mineral assemblages and luminescent characteristics of the cements it would be possible to predict the approximate redox potentials of the pore water in which the cement formed. In practice this involves recognising different luminescent intensities and the minerals associated with these zones.

Figure 2.1. A catenary diagram modeling the theoretical redox conditions under which different cathodoluminescence cement zones form (after Carpenter and Oglesby 1976); with the luminescence characteristics being determined by the availability of activator and quencher ions.



Zone I	MnO_2, FeOOH, $CaCO_3$	Dead
Zone II	FeOOH, $(CaMn)CO_3$	Bright
Zone III	FeOOH, $(CaFeMn)CO_3$	Dull
Zone IVa	FeS_2 $(CaMn)CO_3$	Bright
Zone IVb	$(Fe,Mn)S_2$, $CaCO_3$	Dead

In this study five luminescence levels were recognised:

a) Very bright

b) Bright

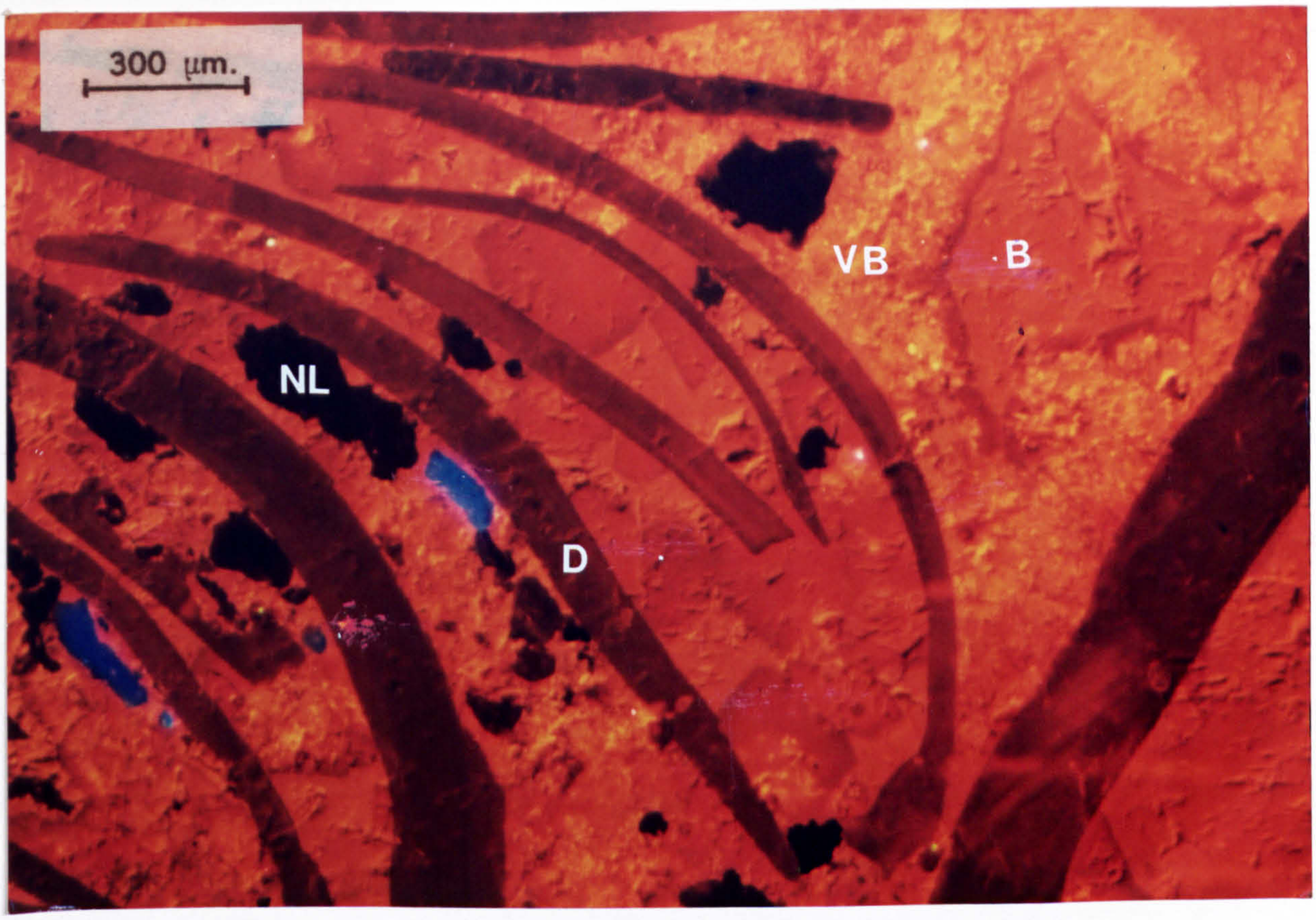
c) Medium

d) Dull

e) Not luminescing

and these are illustrated in plate 2.1.

Plate 2.1. An example of luminescence zones in calcite; very bright (VB), bright (B), dull (D) and not luminescing (NL).



Recently there has been much controversy about the exact nature of this banding pattern. In particular the influence of other quencher ions has been postulated, notably nickel, cobalt and lead (Miller pers. comm. 1984); thus it is not always clear from the luminescence characteristics alone what dissolved ions were available for incorporation into the growing crystal. Dickson (1983) has shown that the speed of crystal growth may also determine its luminescent characteristics, as a slow growing crystal tends to sweep aside potential impurities. Thus whatever the pore water chemistry associated with a slow growing crystal, its luminescent characteristics would be dull and it would mimic zone 1 cements of Carpenter and Oglesby (1976) (figure 2.1) due to the absence of both activators and quenchers.

In this study whilst the problems of defining exactly what causes luminescence are recognised, it is assumed for simplicity that the critical factors influencing CL. characteristics are the relative proportions of ferrous and manganous ions in the crystals. It is further assumed that this ratio broadly reflects the amount of reduced iron and manganese available for incorporation into the calcite at the time of precipitation and therefore reflects the changing redox potentials of the pore water system. Obviously all this is seen against the uncertainty of varying crystal growth rates and the effects of other activator and quencher ions.

(3) Electron optical analysis.

Electron optical analysis was performed on an ISI. 100A scanning electron microscope housed in the British Petroleum Research Laboratories at Sunbury-on-Thames. Analysis of fractured surfaces revealed little detail in either the mudstones or the cemented units. However backscatter analysis (using a Robinson backscatter detector), coupled with an energy dispersive X-ray spectra (EDS) analysis (using an EDAX detector) on polished thin sections were found to be useful, as the combined technique was able to determine the spatial distribution of minerals and elements within the thin sections. It is worth noting that no attempt at quantitative analysis was made, although the working distance was standardized to 20 mm. and thus the EDS spectra are only qualitative. A detailed review of backscatter and EDS analysis is not given here and can be found, if required, in Scott and Love (1983) and Loretto (1984).

Section 2.3. X-Ray diffraction and bulk mineral analysis.

X-ray diffraction was undertaken in this study for two reasons:

(a)To provide whole rock data for general mineral analysis.

(b)To provide specific data on the clay minerals suites.

(i) Total mineral analysis.

About 20 gms. of each sample was prepared for bulk mineral analysis by X-ray diffraction. Initially each rock sample was crushed and the resulting powder passed through a <63 um. sieve. Finally 20ug. of the sample was wetted with distilled water and part was smeared on to a 2x2 cm. glass slide.

The resulting whole rock sample was then analysed in a Philips X-ray diffractometer, using copper K alpha radiation at an operating current of 40 mA. and a voltage of 40 Kv. The diffractometer was set to scan at one degree two theta per/minute, and each sample was analysed from 3-60 degrees two theta.

The resulting peaks were identified using the tables in Brindley and Brown (1980) and the samples were found to contain varying quantities of:- quartz, calcite, pyrite, fluorapatite, dolomite and minor amounts of K feldspar. Summary whole rock XRD. traces are presented in figure 2.2. and the d spacings and relative intensities of the Bragg reflections for the major component minerals are given in table 2.1.

Figure 2.2. Examples of whole rock XRD. spectra from Aust 2, Wainlode 1a and Wainlode 13a. Showing characteristic X-Ray spectra (using copper K alpha radiation) of the common "sand grade" minerals e.g. quartz, dolomite, phosphate, calcite and pyrite.

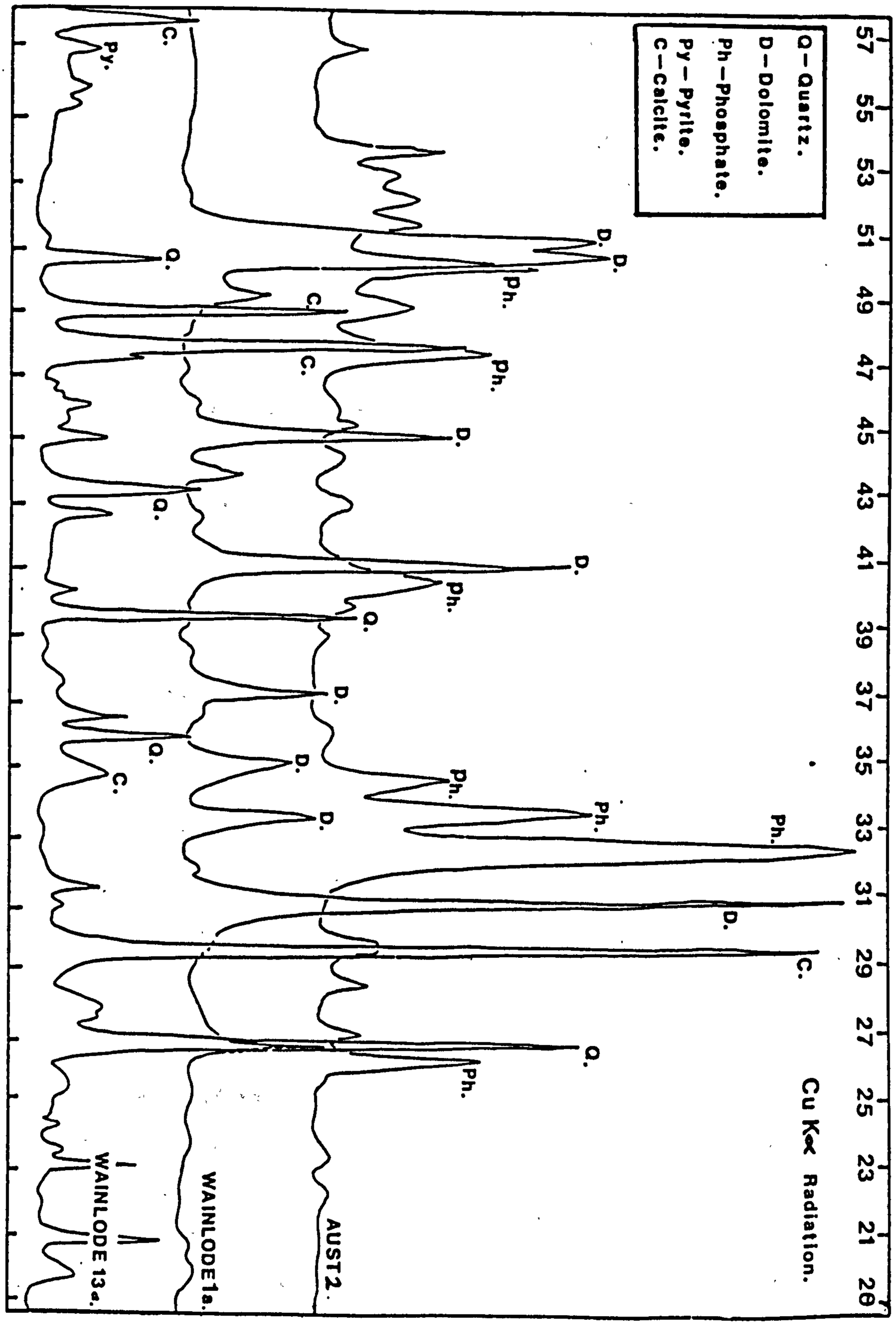


Table 2.1.

Quartz

dÅ	I	(hkl)
3.035	100	(104)
2.495	14	(110)
2.285	18	(113)
2.095	18	(202)
1.913	17	(108)
1.875	17	(116)
1.375	11	(203)

Calcite

dÅ	I	(hkl)
4.263	5	(100)
3.343	100	(101)
2.458	12	(110)
2.282	12	(102)
1.817	17	(112)
1.541	15	(211)

Pyrite

dÅ	I	(hkl)
2.709	85	(200)
2.423	65	(210)
2.2118	30	(215)
1.915	40	(220)
1.6332	100	(311)

Fluorapatite

dÅ	I	(hkl)
3.442	40	(002)
2.800	100	(211)
2.772	55	(112)
2.702	60	(300)
1.937	25	(222)
1.837	30	(213)

Dolomite

dÅ	I	(hkl)
2.886	100	(104)
2.192	30	(113)
1.804	20	(108)
1.786	30	(116)
1.781	30	(009)

(ii) Clay mineral and soluble carbonate analysis.

In order to determine the amount of soluble carbonates and break down the carbonate rich units into an insoluble detrital fraction, the remaining crushed, <65 um sample was weighed, and decalcified in 1% ethanoic acid. On completion of this reaction the sample was carefully washed with warm distilled water (to remove any soluble calcium acetate),

air dried (at 100°C) and reweighed. The recorded weight loss was assumed to approximate to the amount of soluble carbonate originally present in the sample and is shown graphically in appendix 3.

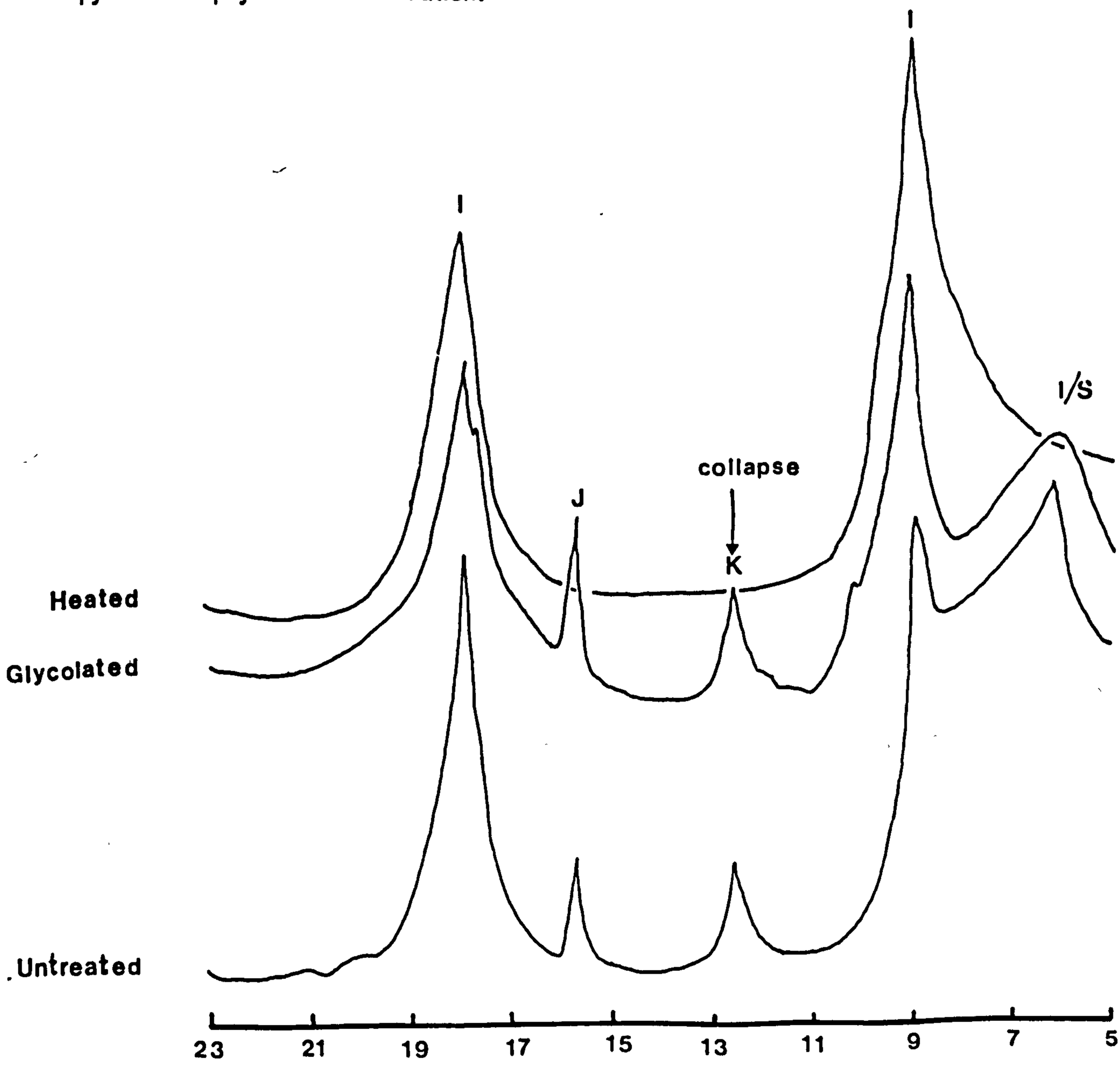
To separate the <2um. fraction the decalcified sample was rewetted with a 0.1% sodium hexametaphosphate solution (to prevent the clays flocculating) and vigorously hand shaken for 30 seconds to suspend the fine fraction. The resulting suspension was then transferred to a centrifuge tube and spun, for a short time to compact the >2um estimated spherical diameter (e.s.d.) fraction. The remaining suspension was transferred to a second centrifuge tube and spun for a second, longer time to compact the <2 um. e.s.d. fraction. Centrifuge spinning times were calculated using a modified version of Stoke's law (Hathaway 1956). Finally the supernatant was discarded and approximately 20 ug. of the compacted, <2um. e.s.d. fraction was smeared on to a 2x2 cm. glass slide and air dried to produce an (001) orientated sample.

The <2um. sample was then analysed in a Philips X-ray diffractometer, using Cu K alpha radiation, operating at 40 Kv. and 40 mA. and scanned from 3-30 degrees two theta at one degree two theta per/minute. The resulting data was then transferred to an Apple II microcomputer and stored via a Linkman interface package supplied by J.S. Systems of Reading.

In order to differentiate between the mixed layer clay minerals and the standard clays the samples were treated with ethylene glycol (by placing the air dried, <2um., orientated sample in a desiccator above ethylene glycol and heating it to 60°C. The ethylene glycol replaces the interlayered water of the "mixed layer clays" thereby expanding their lattice parameters. Consequently after X-ray diffraction their d spacings increase, relative to the air dried samples, "making the mixed layer minerals" easy to distinguish from the standard clays (see figure 2.3). X-ray diffraction of the glycolated samples was carried out using the same operating conditions as the air dried samples (see above).

Finally in order to collapse the mixed layer peaks and differentiate between the kaolinite (001) and (002) peaks and the chlorite (002) and (004) peaks the <2um. sample was heated to 550°C (which causes the kaolinite peaks if present to collapse). The heat treated sample was then reanalysed at the standard <2um. operating conditions (see above).

Figure 2.3. X-Ray spectra of the <2 um. fraction from Sedbury 8 (fossiliferous mudstone facies), showing the effects of different chemical treatments (glycolation and heating) on the clays. The dominant clays are illite (I), illite/smectite (I/S) and kaolinite (K). Glycolation has caused the expansion of the illite/smectite mixed layer phase, and heating to 550°C. has caused the kaolinite peak to collapse. The peak labeled J is jarosite which is produced as a secondary byproduct of pyrite and phyllosilicate oxidation.



The <2um. treated and untreated traces were analysed using the Apple II/J.S. Systems software, and the resulting peaks were assigned to the different clay minerals using the tables in Brindley and Brown (1980) and Hower (1981). The characteristic d spacings, relative peak intensities and Bragg reflections of the clay minerals are given in table 2.2. Details of all the glycolated traces are presented with the logs in appendix 3. The <2um. samples were found to contain: illite, kaolinite, "mixed layer illite/smectite" and minor amounts of chlorite.

Table 2.2

Illite			Kaolinite		
dÅ	I	(hkl)	dÅ	I	(hkl)
10.08	100	(001)	7.16	100	(001)
5.04	70	(002)	4.46	40	(020)
4.49	90	(020)	4.36	50	(110)
4.35	27	(111)	4.18	50	(111)
3.66	60	(112)	3.573	100	(002)
3.356	>100	(003,022)	3.372	40	(111)
2.56	60	(201)			

Chlorite		
dÅ	I	(hkl)
14.15	80	(001)
7.05	100	(100)
4.72	60	(003)
3.54	10	(004)
2.83	40	(005)
2.59	50	(202)

Randomly interstratified, mixed layer illite/glycol smectite (after Hower 1981), assuming classical 40% interlayer illite (however note text comments below.

dÅ	I	(hkl)
8.92	20	(001)/(002)
5.49	20	(002)/(003)

Nadeau *et al.* (1984) have suggested that classical analysis of interlayered clays (Reynolds and Hower 1970, Hower *et al.* 1976 and Hower 1981) which use X-ray diffraction to measure the different proportions of illite in the individual illite smectite mineral may be incorrect. As Nadeau *et al.* (1984) propose that the characteristic low angle 2 theta peaks of glycolated mixed layer samples are a characteristic of interparticle effects and nothing to do with clay interlayering. In the light of this problem detailed study of the "mixed layer" phases was not attempted.

Section 2.4. Organic Geochemistry, sample preparation and analysis.

(a) Sample selection and preparation.

Sample selection was governed by a number of specific criteria:

i) To select a number of samples from each tectonic province - i.e. both the Worcester Graben and Bristol Channel Trough.

ii) To select samples at various distances from probable emergent areas, in order to ascertain if there are provenance variations within the organic matter.

iii) To check a number of samples within each geographic area to ascertain the thermal history of each basin and local area.

iv) To obtain relatively unweathered material.

To fulfill these obligations samples were analysed from: Watchet Harbour 15, Penarth 3 and Burton Row 8 from within the Bristol Channel Trough; and from Stowell Park 9, Aust 8 and Westbury Garden Cliff 15 from within or close to the edge of the Worcester Graben.

In order to analyse the samples they were first ground to a powder in a Tema mill. This powder was then transferred to a soxhlet, and the soluble organic matter was extracted using dichloromethane and methanol (in a ratio of 9/1). The aliphatic hydrocarbons were then separated from the polar fraction by thin layer chromatography (on a silica plate using hexane as the eluting solvent.

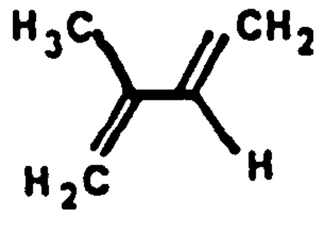
(b) Sample analysis and compound recognition.

The organic matter analyses were carried out in the Organic Geochemistry Unit at Bristol University using gas chromatography (gc.)(a Carlo Erba 2150 gc. equipped with 25m. OV-1 WCOT flexsil capillary column) and gas chromatography - mass spectrometry (gc-ms.)(on a Finnigan 4000 coupled to Carlo Erba gc. equipped with flexsil OV-1 column and interfaced to INCOS 2300 data system).

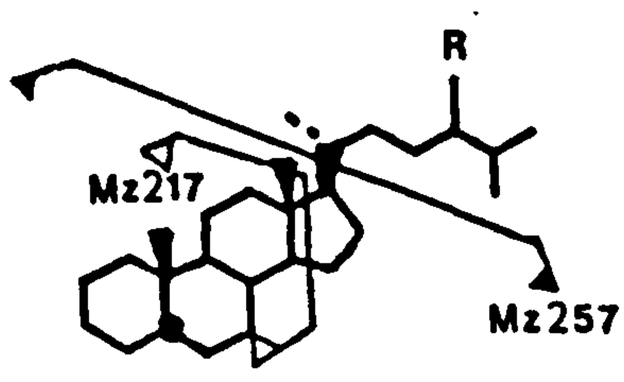
Individual compounds were characterized from a combination of their gc. retention times, mass spectra and mass fragmentographic (MF) responses by reference to literature or standard mass spectra. This technique was not intended to be quantitative instead the data produced is only qualitative as no internal standards were added. The common characteristic compound structures are shown in figure 2.4 for the significant organic matter components in the Westbury Formation.

Figure 2.4. The diagram shows the stereochemistry of the common organic biomarkers preserved in the Westbury Formation, and the characteristic mass fragments of the molecules which are produced after stepped heating in a gas chromatograph

Isoprenoid



Steranes.

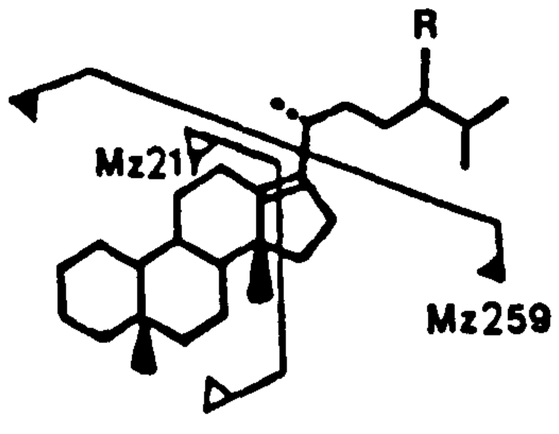


R– H – C_{27}

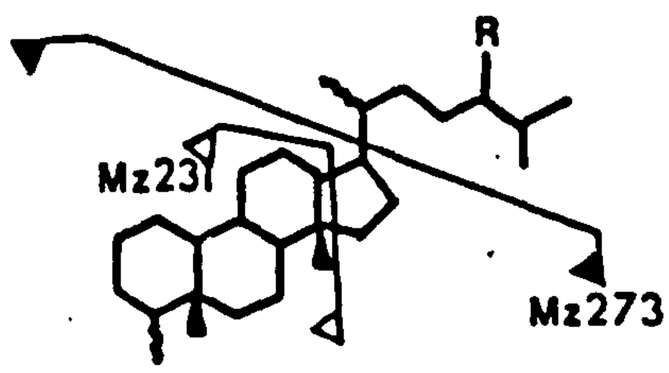
R– CH_3 – C_{28}

R– C_2H_6 – C_{29}

Sterenes.



4–Methylsteranes.

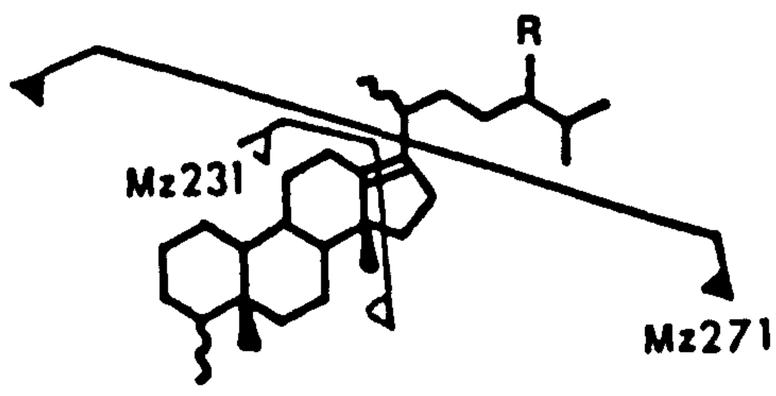


R – H – C_{28}

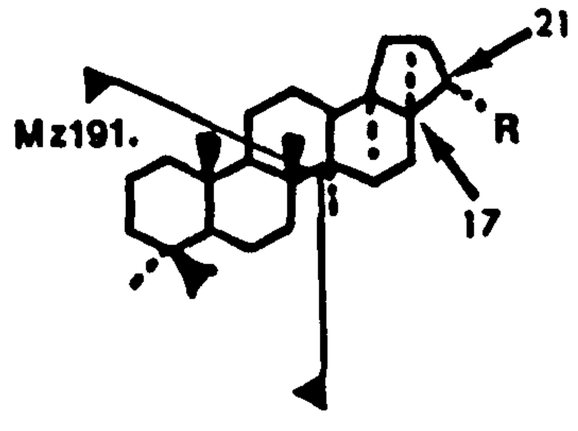
R – CH_3 – C_{29}

R– C_2H_6 – C_{30}

4–Methylsterenes.



Hopanoids.



CHAPTER 3. FACIES ANALYSIS.

Section 3.1. General lithological variation within the Westbury Formation and an introduction to the facies present.

The Westbury Formation consists of alternating black mudstones and carbonate horizons, with the mudstones comprising approximately 80% of the sequence.

The mudstones contain silt grade quartz, K feldspar, up to 10% organic matter, illite, illite/smectite and kaolinite and at some horizons decalcified shell material. The carbonate units contain shell debris, sand grade quartz, K feldspar, <0.1% organic matter, <1% clays, <15% phosphate and pore filling calcite.

The facies present within alternating limestone/mudstone sequences are notoriously difficult to classify, as they often require a plethora of names to describe the basic facies types. In this study 6 major facies are recognised in the Westbury Formation

i) Mudstones.
ii) Fossiliferous mudstones.
iii) Calcareous sandstones.
iv) Calcarenaceous sandstones.
v) Packstones.
vi) Wackestones.

These facies often grade into one another and are frequently modified by diagenesis, thus distinction between end members is often fairly arbitrary.

Detrital mudstone classification is fairly straight forward and has been reviewed by Potter *et al.* (1980) and Pettijohn *et al.* (1982). In this study two detrital mudstone facies have been recognized:

a) Mudstones.

b) Fossiliferous mudstones.

The Westbury Formation mudstones contain no carbonate cement and have a grain size of <63 um., with the latter comprising: quartz, illite, "mixed layer illite/smectite", kaolinite and organic matter. The principle difference between the two facies is that the fossiliferous mudstones contain decalcified fossil debris, whilst the "true" mudstones do not.

The 2 dominant arenaceous facies are:

a) Calcareous sandstones.

b) Calcarenaceous sandstones.

Both facies contain carbonate and allochthonous arenaceous debris, and are distinguished from one another by having different proportions of these two components. Units that contain >50% quartz, K feldspar, <10% authchthonous carbonate debris and pore filling calcite are termed calcareous sandstones (Pettijohn *et al.* 1982); whilst units that contain >30% quartz, >30% autochthonous carbonate debris and a pore filling calcite are termed calcarenaceous sandstones (Pettijohn *et al.* 1982). Unfortunately these definitions are frequently complicated by diagenetic processes; for instance the carbonate maybe secondarily replaced by pyrite, in which case no change is made to the basic facies code, however to distinguish them from the normal arenaceous units they are prefixed pyritic.

The two dominant carbonate facies are:

a) Packstones.

b) Wackestones.

Both facies are carbonate dominated and may contain a subsidiary detrital component (after Dunham 1962 and Wilson 1975). Both facies codes

Plate 3.1. Symmetrical wave ripple lamination.
Symmetrical, predominantly straight crested ripple marked sandstone, with rare bifurcating crests (arrowed), from Westbury 1. Coin3 cm.

Plate 3.2. Calcareous sandstone (p.p.l.).
Calcareous sandstone with abundant phosphatic debris, from Carrefour 8. Medium grade sand (Q) and vertebrate derived phosphatic debris (Ph) in a non-ferroan calcite cement (NFC).

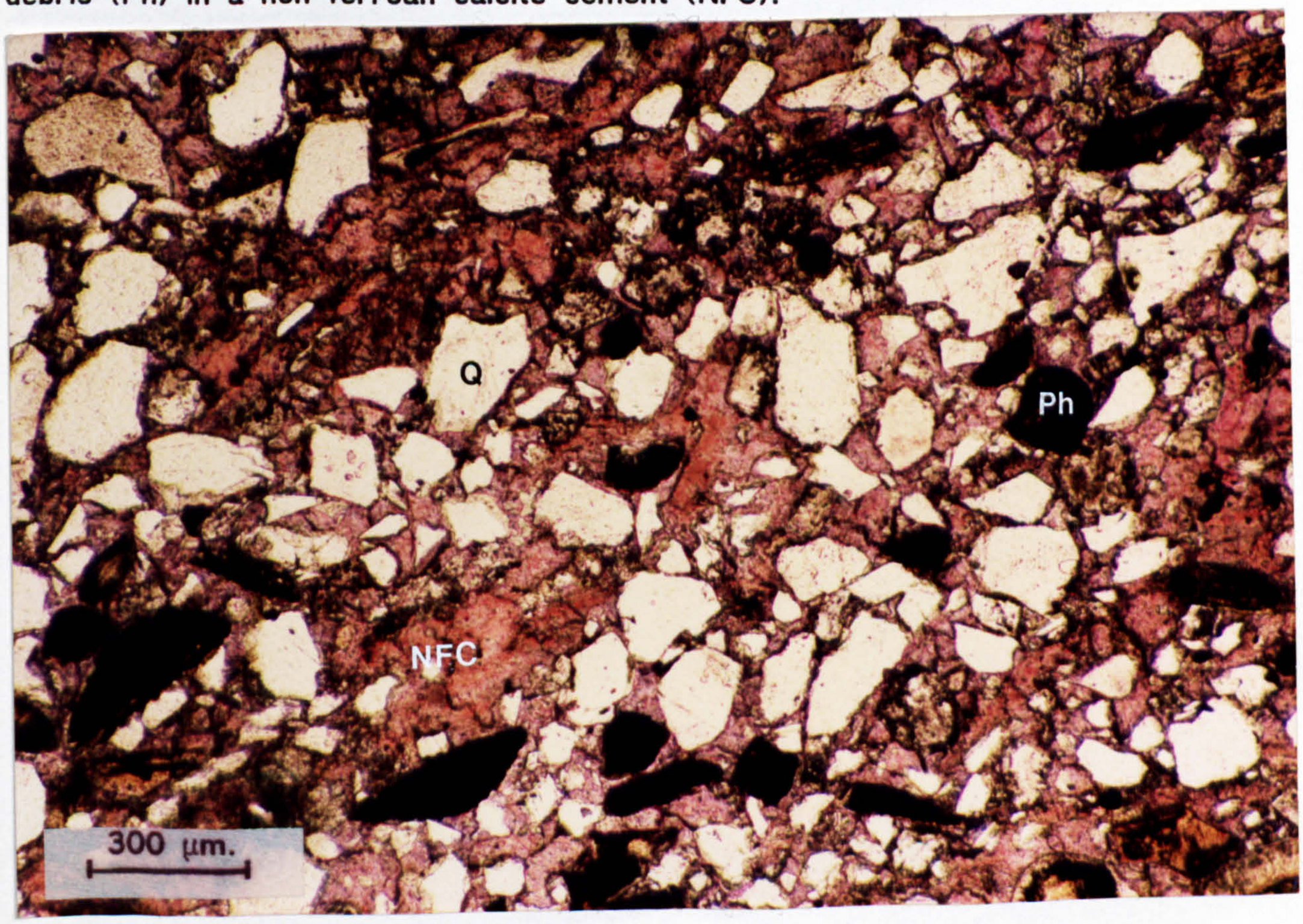


Plate 3.3. Calcareous sandstone (CL.).
Calcareous sandstone containing fine sand grade quartz (Q), feldspar debris (K&F) and etched bivalves (Bv, with etching arrowed) within a pore filling bright luminescing calcite, from Wainlode 6. Both K feldspars (K) and orthoclases (F) are present, with the former having well developed overgrowths (also arrowed).

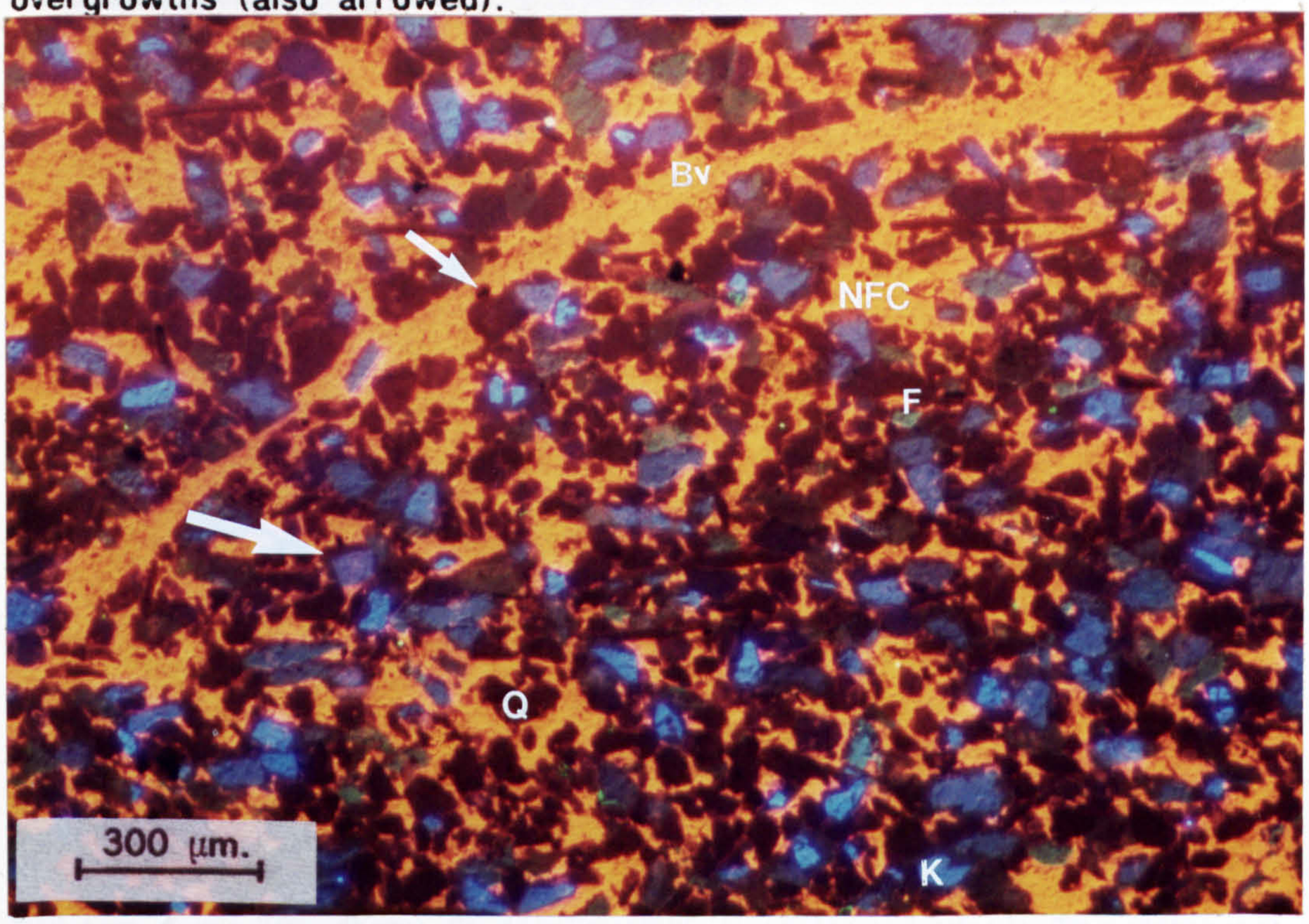


Plate 3.4 Calcareous sandstone (p.p.l.).
Calcareous sandstone from Aust 21. Containing abundant fine sand grade quartz (Q) and a minor component of glauconite pellets (Gl) and detrital micas (M), which are cemented by non-ferroan calcite (NFC). A minor biogenic component includes disarticulated echinoderm plates (E), whose steron system has been partially replaced by pyrite.

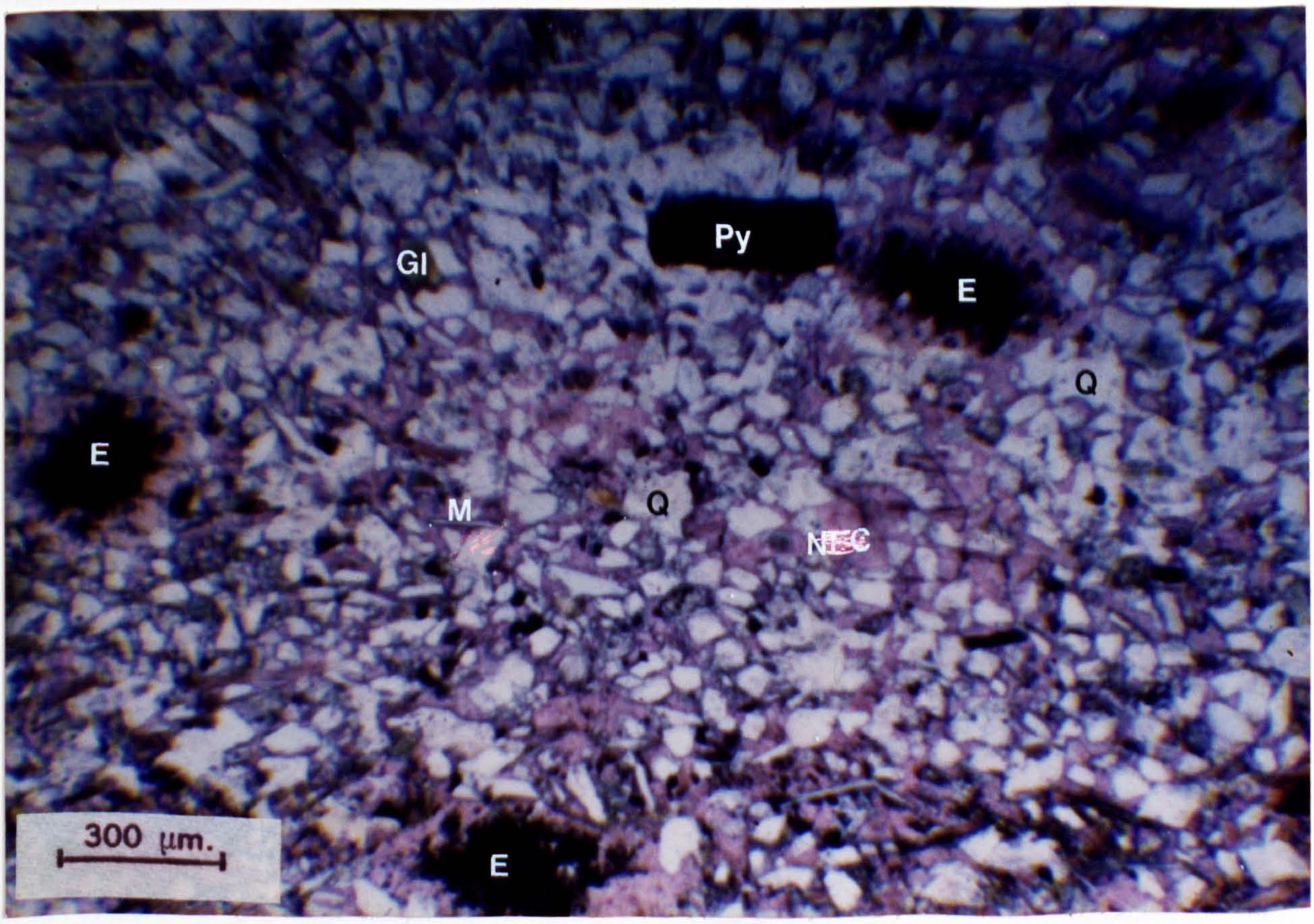


Plate 3.5 Calcareous sandstone, (CL.).
Calcareous sandstone containing detrital sand grade quartz (Q), K feldspars (K) and vertebrate derived phosphate debris (Ph) in a bright luminescing unzoned calcite cement (NFC).

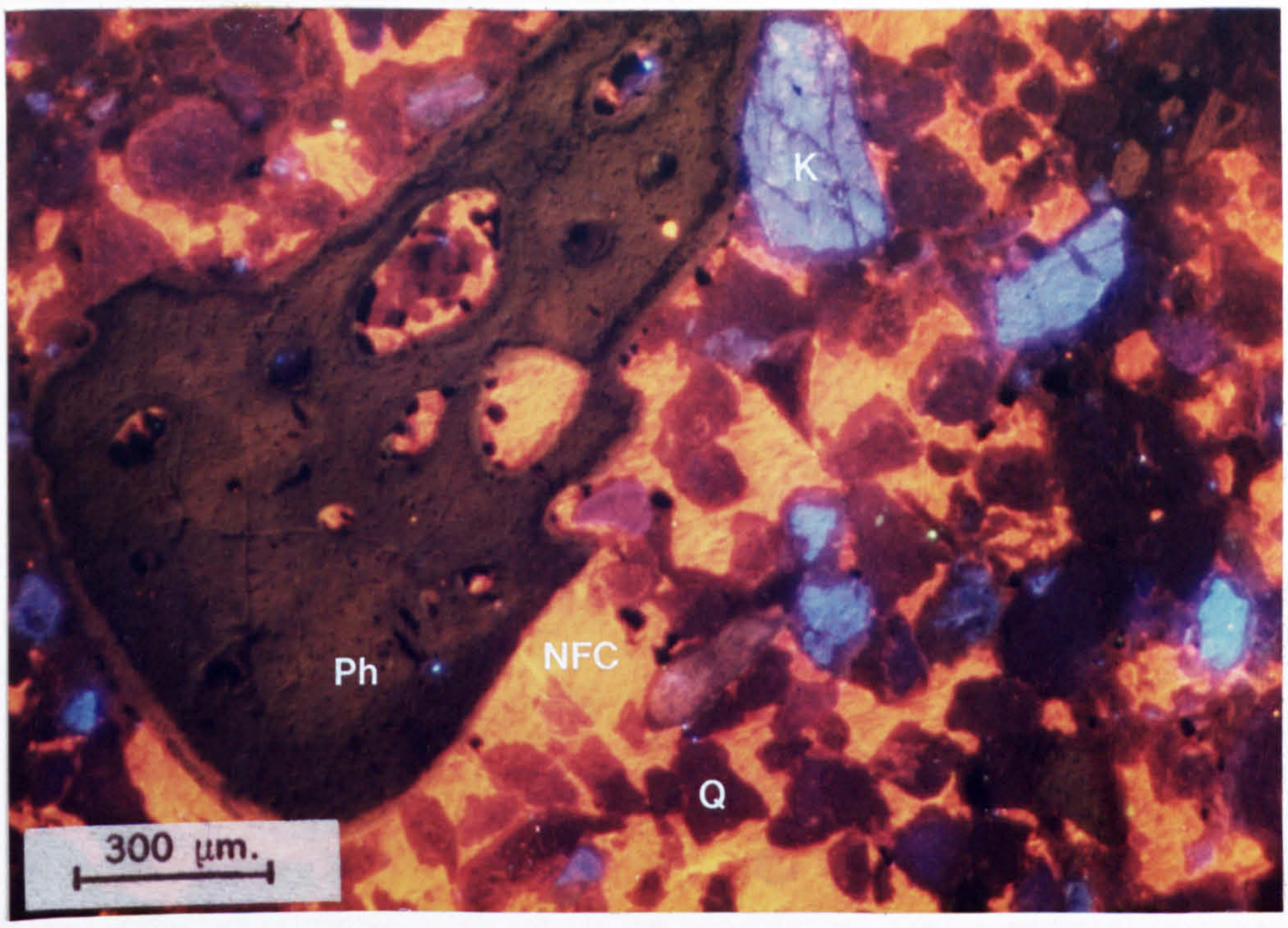
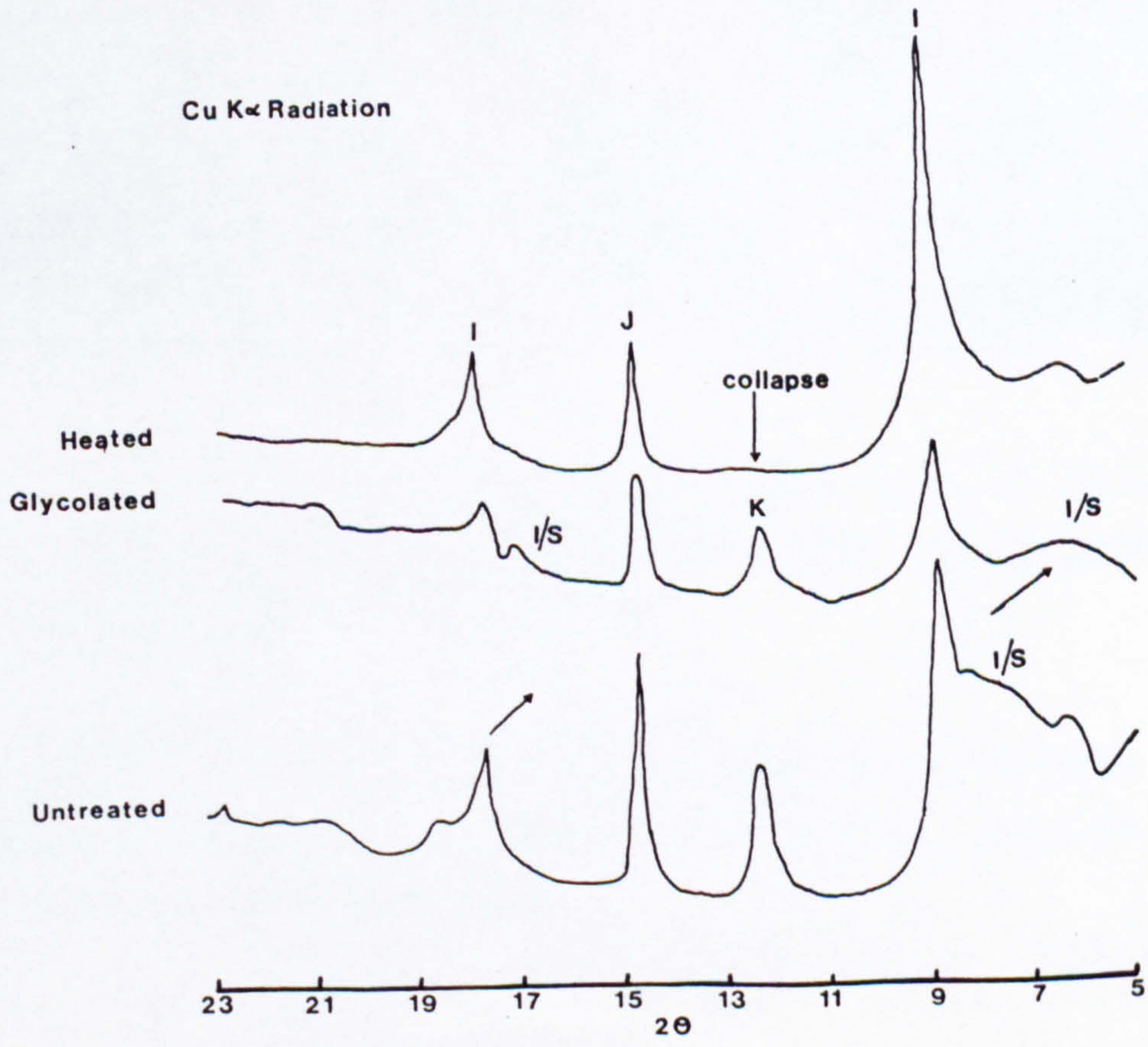
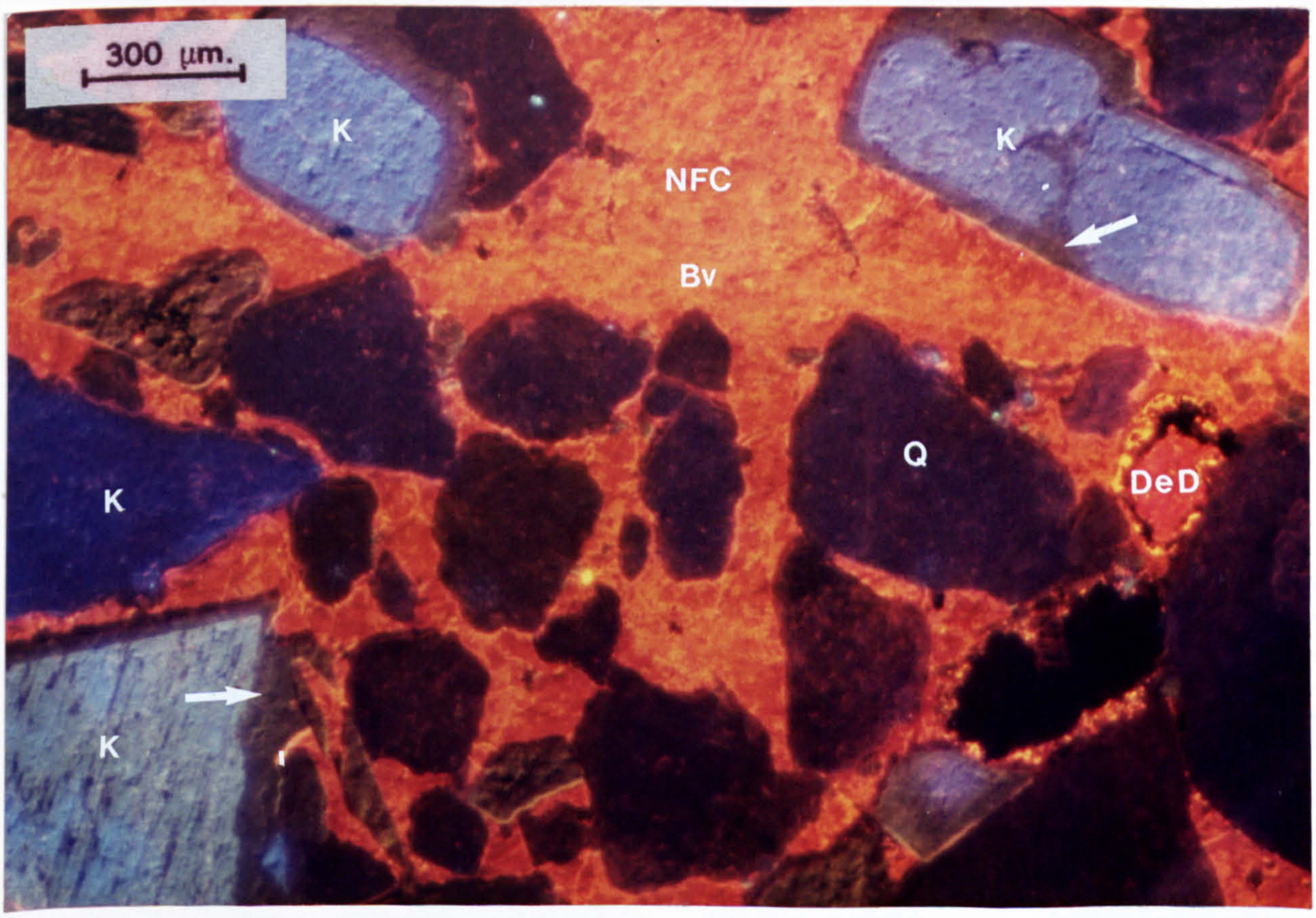


Figure 3.1. X-ray spectra of the untreated, glycolated and heated <2um. fraction from Westbury 21 (calcareous sandstone facies). The dominant clays are illite (I), "illite/smectite" (I/S) and kaolinite (K). Glycolation has caused the expansion of the illite/smectite "mixed layer" phase, and heating to 550 C. has caused the kaolinite peak to collapse. The peak labeled J is jarosite, which is produced as a secondary byproduct of the oxidation of pyrite and phyllosilicates.



The average grain size at most localities (within this lithofacies) is medium/fine sand (e.g. plate 3.2 - plate 3.5), however at Penarth it increases to medium/coarse sand (plate 3.6).

Plate 3.6 Calcareous sandstone (CL.).
Calcareous sandstone, containing medium/coarse, sand grade K feldspar (K) and quartz (Q) grains, in a bright luminescing calcite matrix (NFC), from Penarth 5. The K feldspars have well developed authigenic overgrowths (arrowed). Small de-dolomite (DeD) grains are also present. Within the matrix particularly bright luminescing areas are biogenic fragments e.g. bivalves (Bv).



The main pore filling component is non-ferroan calcite (plate 3.2, plate 3.3, plate 3.4, plate 3.5 and plate 3.6), however locally there may be significant quantities of pyrite (plate 3.7 and plate 3.8).

These sand units tend to have erosive bases and are frequently bioturbated (plate 3.9, plate 3.10, plate 3.11 and plate 3.12), and often the burrows appear scalloped (plate 3.13).

Plate 3.7. Starved ripple from Westbury 9.
Calcareous sandstone with abundant phosphatic debris (arrowed). Large euhedral pyrite crystals (Py) have replaced much of the original calcite.

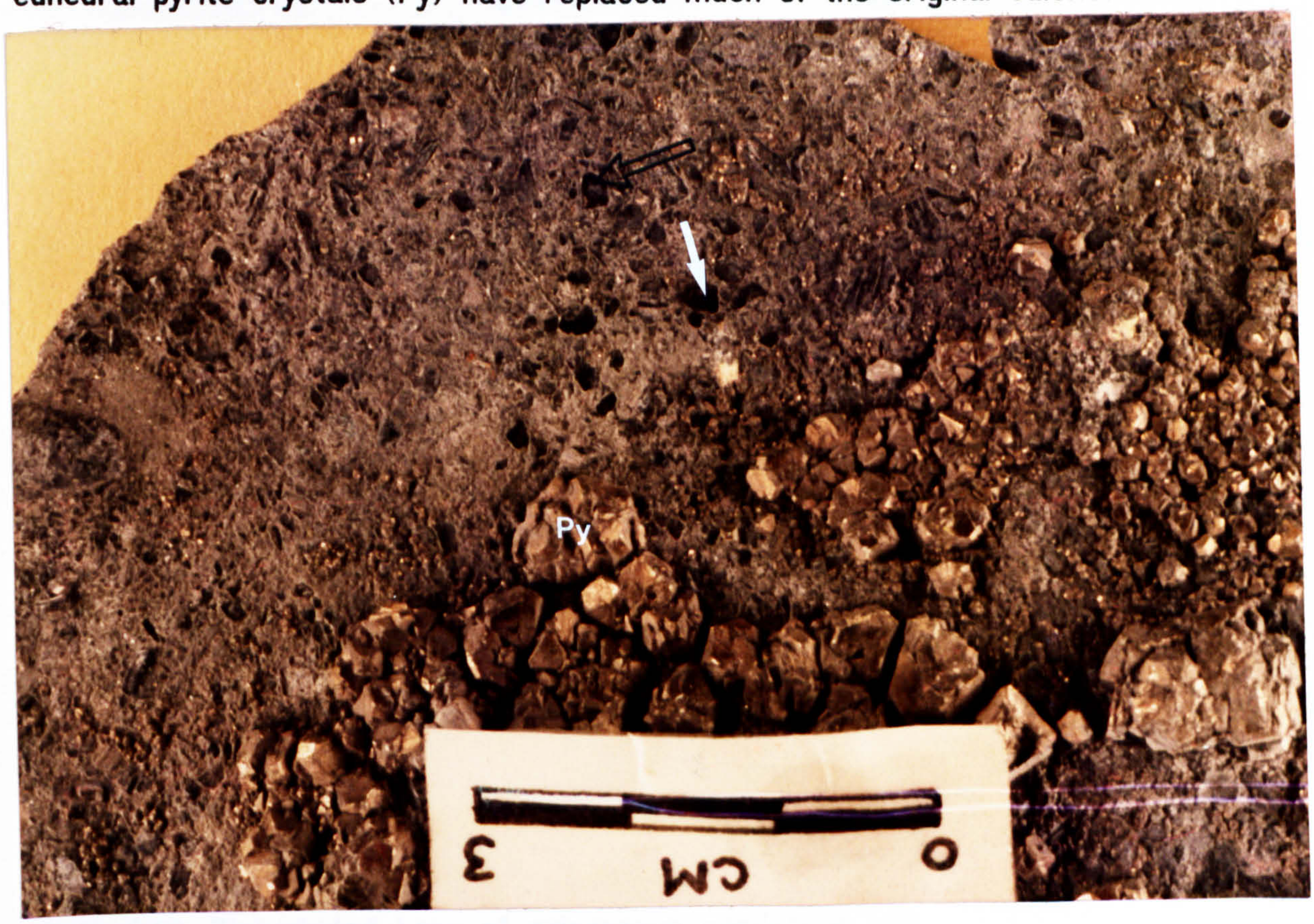


Plate 3.8. Section through Westbury 9 (see plate 3.7), phosphatic sandstone.
Vertebrate derived phosphatic debris (Ph) and quartz (Q) in pyrite matrix (Py).

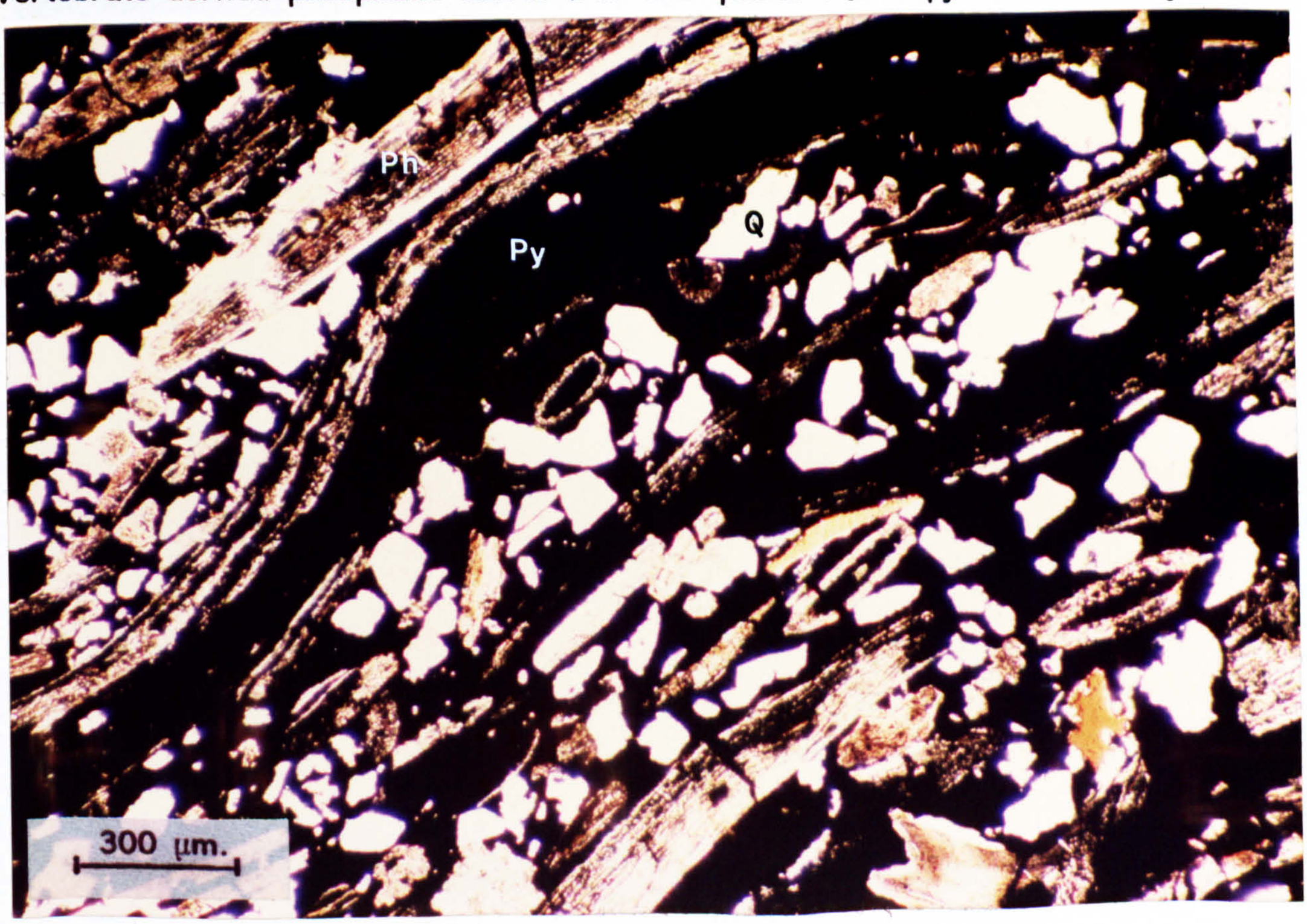


Plate 3.9. Ripple laminated sand (with wavy crests) with trace fossil, from Westbury 3, (coin 2.5 cm.).

Plate 3.10. Bioturbated base of calcareous sandstone unit.
Heavily bioturbated base of calcareous sandstone unit with *Thalassanoides sp.* (Th), from Watchet Harbour 8.

Plate 3.11. Bioturbated base of starved ripple.
Bioturbated base of starved ripple with abundant *Pelecypodichnus sp.* (arrowed), from Aust 21.

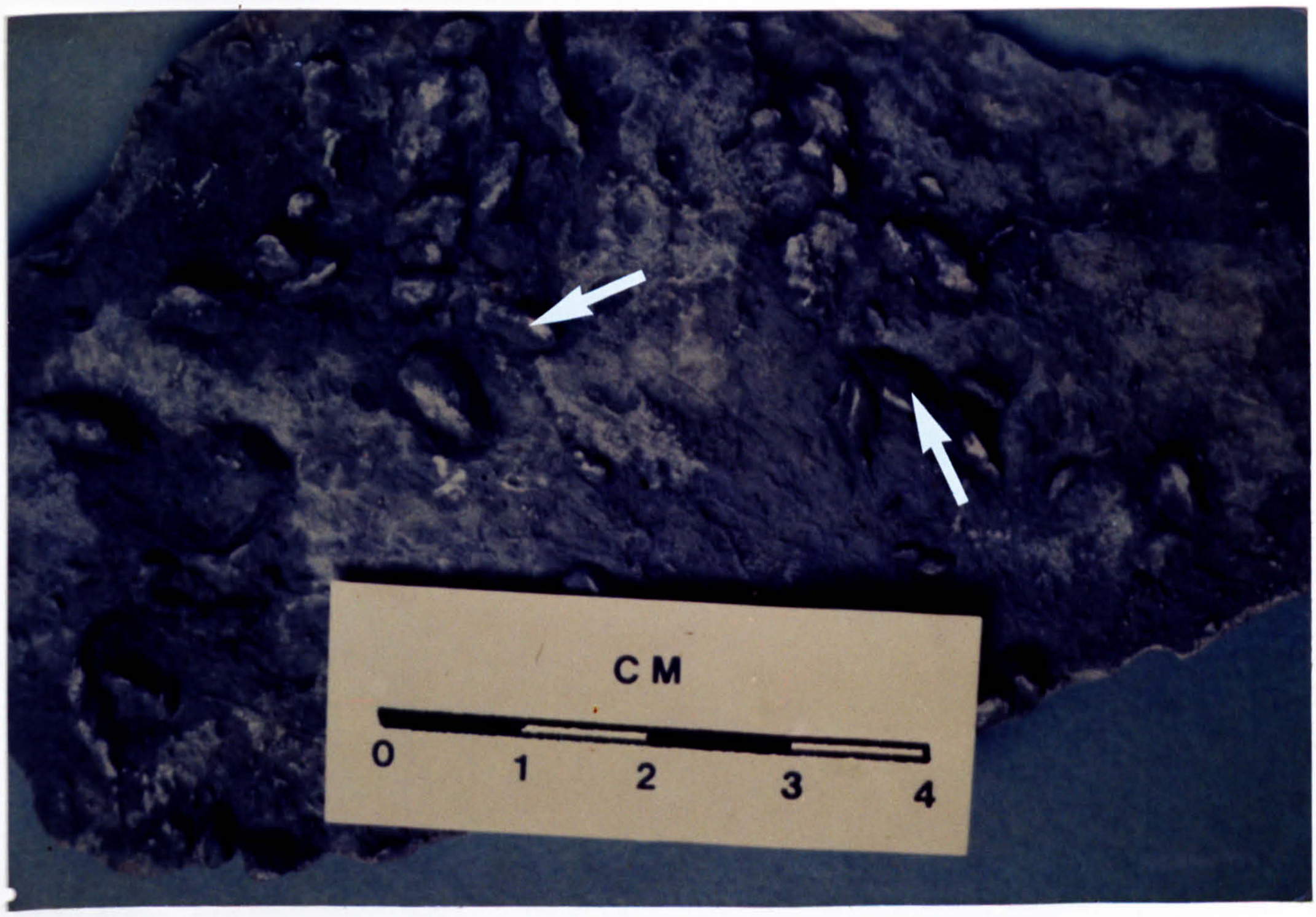
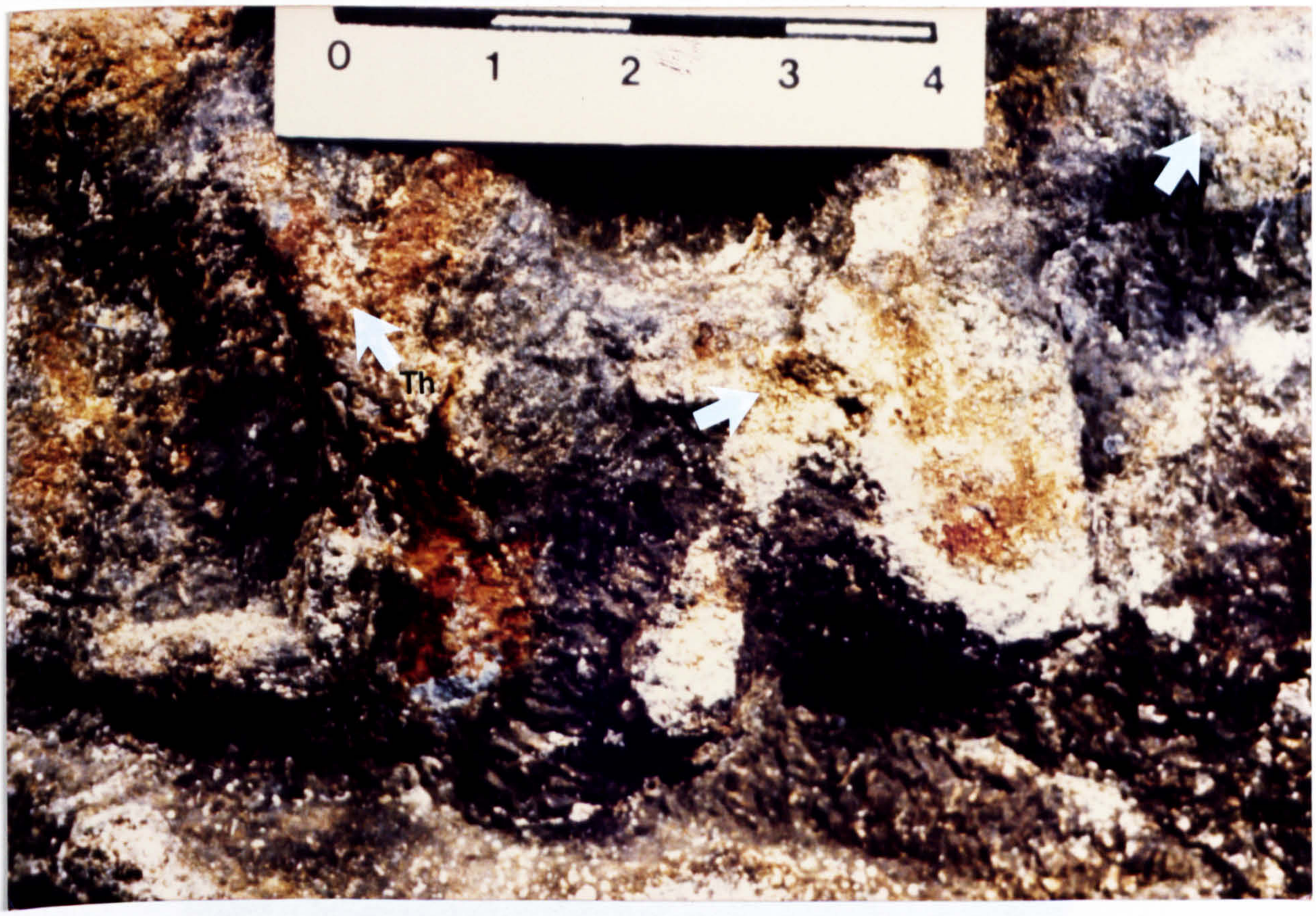


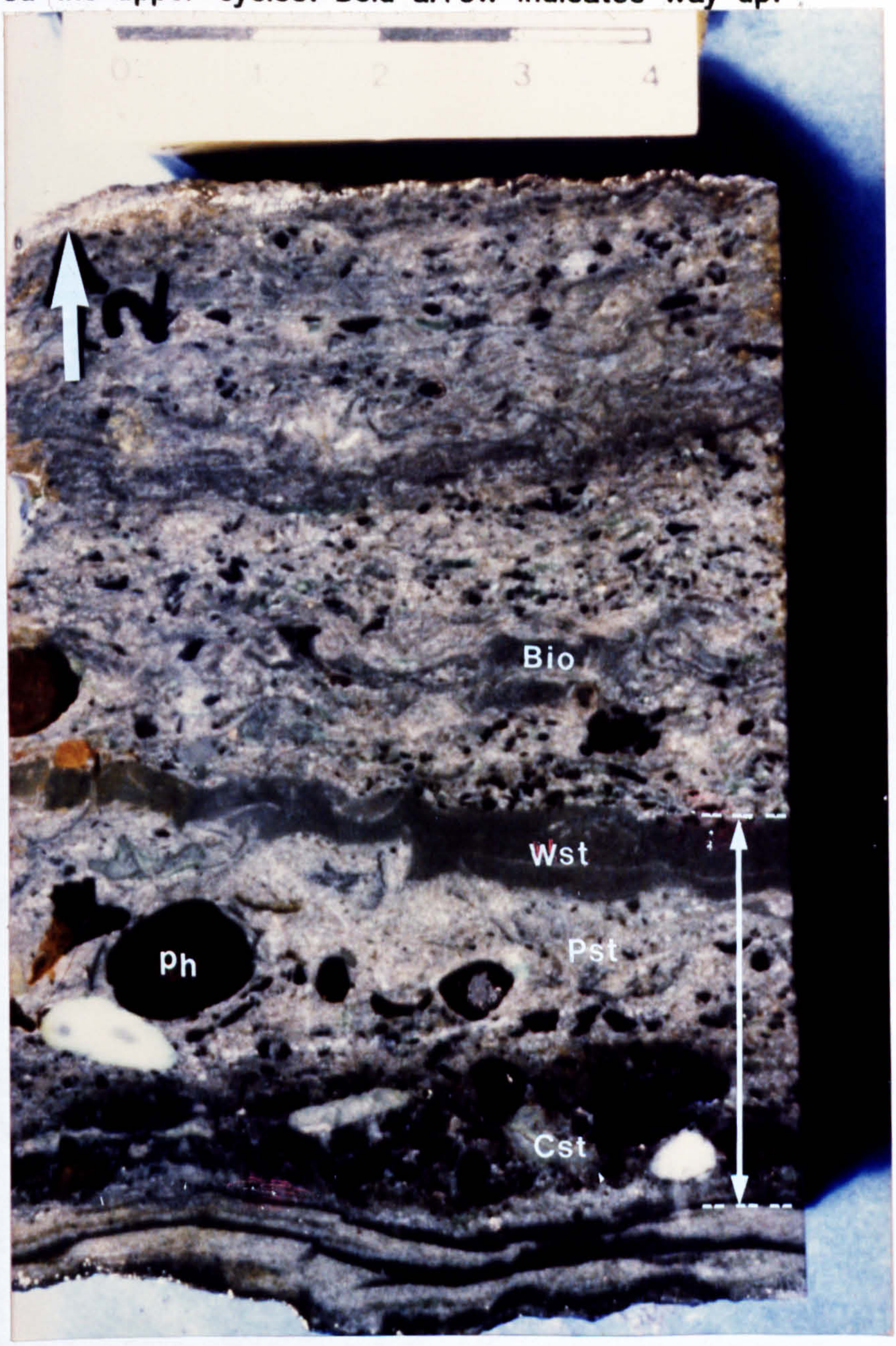
Plate 3.12. Bioturbated base of sandstone unit.
Bioturbated base of sandstone unit with abundant Limulid resting traces (arrowed), from Westbury 4, hammer 40 cm.

Plate 3.13. Scalloped burrows.
Reworked *Thalassanoides sp.* (arrowed Th) burrows on the base of a sandstone unit, from Carrefour 3.



Internally bioturbation has destroyed most of the subtle sedimentological features although gross bedforms and erosion surfaces are still locally recognisable (e.g. plate 3.14).

Plate 3.14. Fining upward cycles separated by erosion surfaces.
Bioturbated, stacked fining upward cycles separated by erosion surfaces, from Wetmoor 2. Each cycle (arrowed) contains a conglomeratic calcareous sandstone at its base (Cst), with quartz and coprolites, which fines up into a calcareous packstone and ultimately into a wackestone. The packstone and calcareous sandstone microfacies are intensely bioturbated (Bio); bioturbation has obscured the upper cycles. Bold arrow indicates way up.



Three main ripple types are preserved in the calcareous sandstones:

a) Symmetrical ripples (plate 3.1), with wavelengths up to 10 cm., with straight to undulating sharp crests (plate 3.9), which occasionally bifurcate and have concentrated convex up bivalve debris in their rounded troughs (plate 3.15). The ripples are orientated north-west south-east (Kelling and Moshriff 1977).

b) Symmetrical ripples with reworked, rounded, terraced ripple crests (which are curved in plan view), have rounded troughs, convex-up bivalves on their base and have wavelengths up to 8 cm. (plate 3.16 and plate 3.17).

c) Starved ripples in a predominantly shale sequence (plate 3.18).

Plate 3.15. Symmetrical ripples.
Symmetrical ripples with reworked convex-up bivalve debris (arrowed) in the rounded ripple troughs, from Westbury 5, (coin 2.5 cm.).

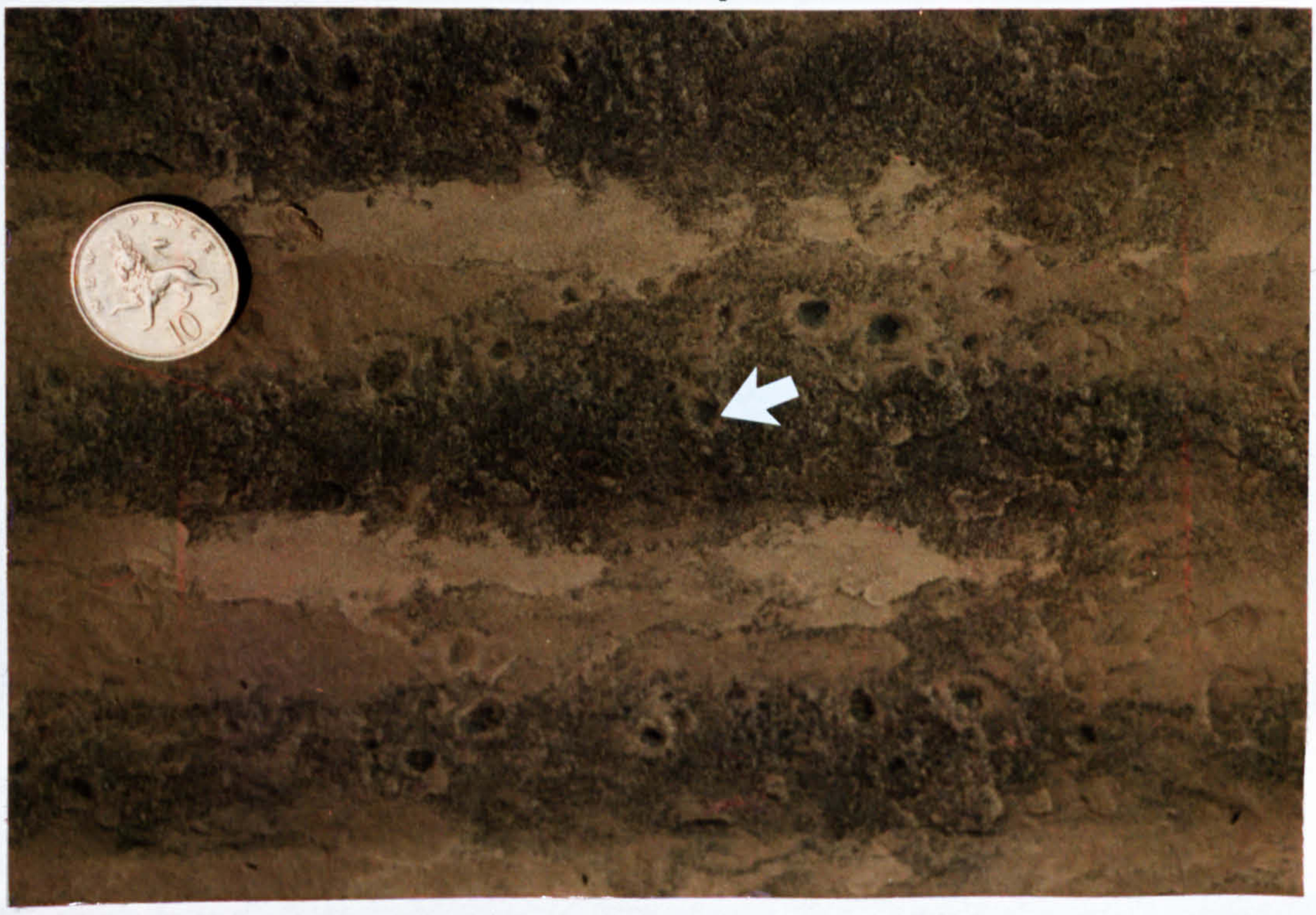


Plate 3.16. Symmetrical ripples with partially reworked crests and terraced edges (arrowed), from Westbury 3.

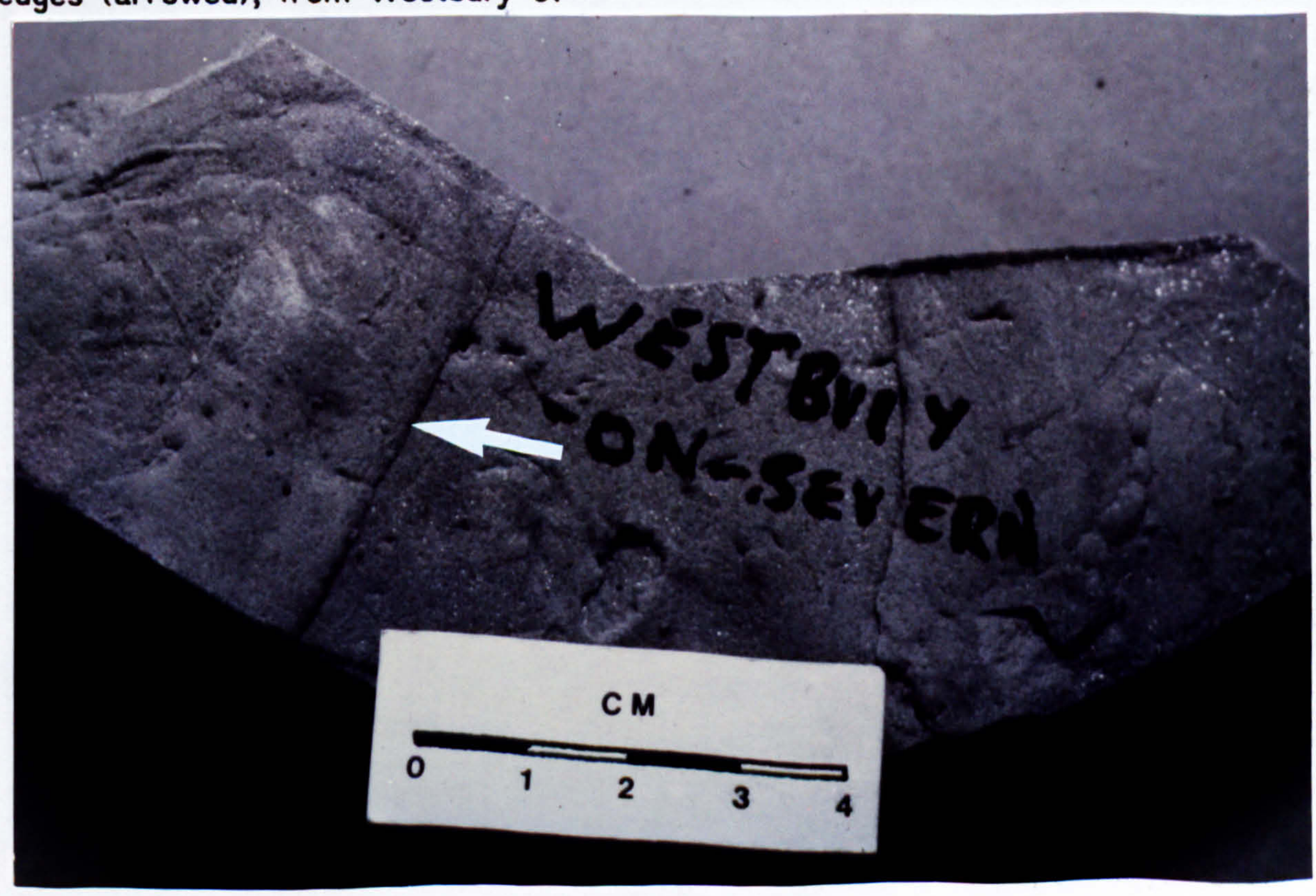


Plate 3.17. Base of symmetrical ripple unit shown in Plate 3.16.
Prominent convex-up bivalves (arrowed) on base of calcareous sandstone from Westbury 3.

Plate 3.18. Starved sand ripples.
Starved sand ripples (arrowed) in a predominant shale sequence, from Westbury 10.

The latter being particularly interesting, as two forms are present:

i) Elongate (in longitudinal section), semi-circular (in cross section) scour casts with horizontal internal laminae (figure 3.2), helical striae and convex up disarticulated bivalves (plate 3.19) on their sides and base.

ii) Lenticular, symmetrical, bioturbated ripples with convex-up bivalves and tool marks on their bases (plate 3.20).

Figure 3.2. Diagramatic cross-section through scour cast, showing horizontal lamination at top, with "channel fill" lamination and convex-up bivalves on the base.

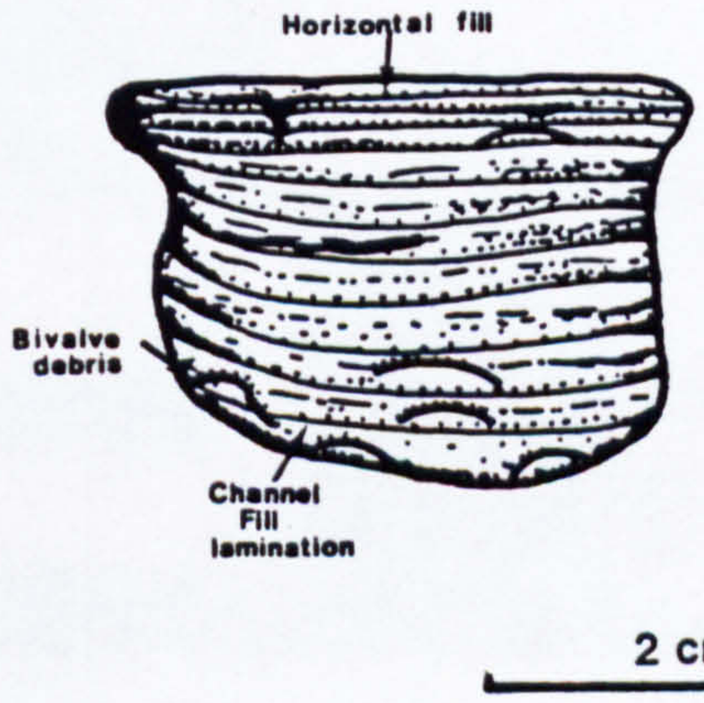


Plate 3.19. Basal view of scour cast.
Basal view of elongate, hemispherical, scour cast, from Aust 3. With helical striae on its sides (arrowed S) and convex up, disarticulated bivalves on its base (arrowed Bv).

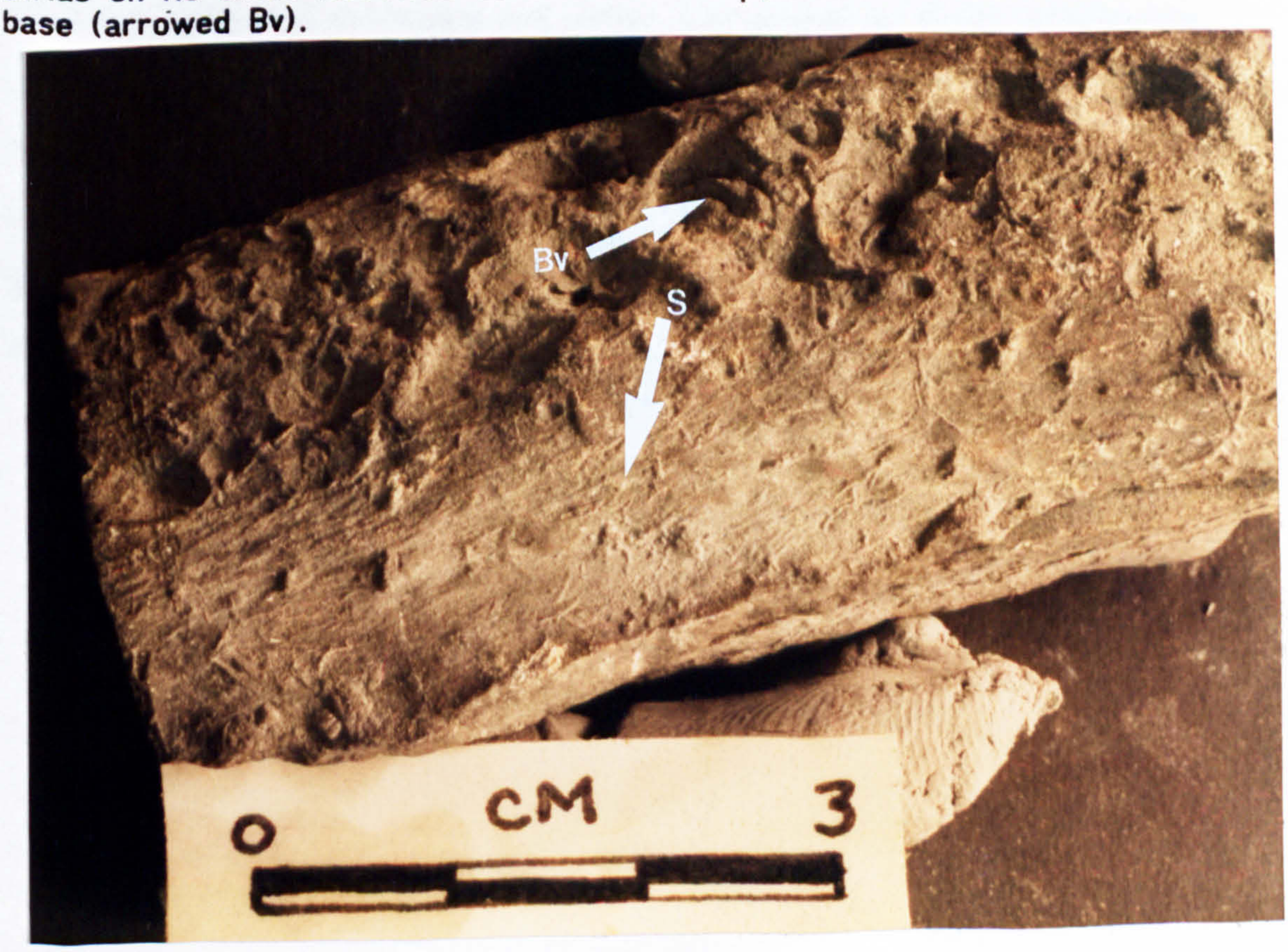
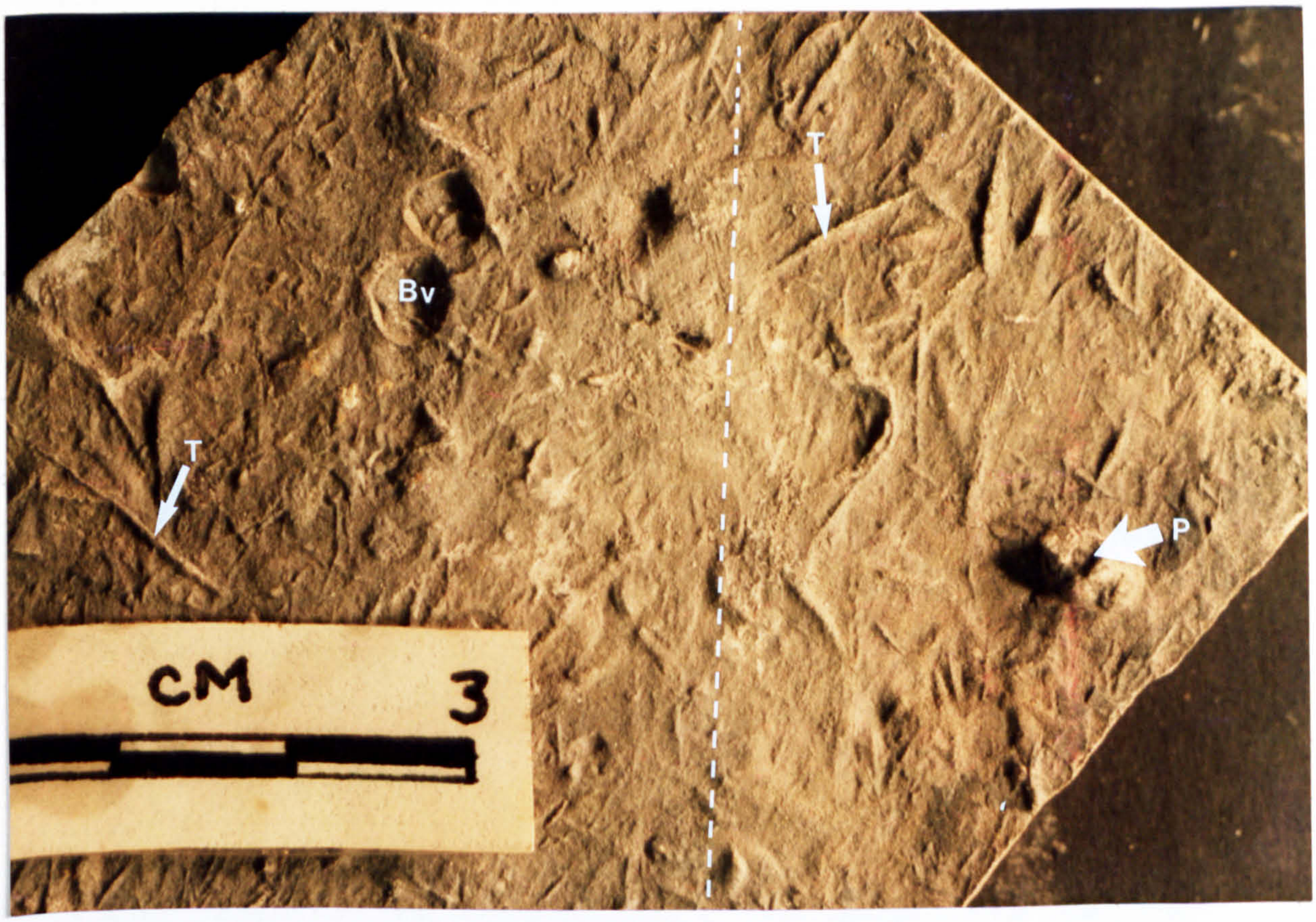


Plate 3.20. Basal view of lenticular ripple.
Basal view of lenticular ripple with tool marks (arrowed T) on either side of the ripple crest (dotted line), from Aust 27. On the base of the ripple convex-up bivalves (Bv) and *Pelecypodichnus sp.* burrows (arrowed P) are present.



Euhedral, dull luminescing K feldspar overgrowths are present on some of the bright luminescing K feldspar grains (e.g. plate 3.3 and plate 3.6). These K feldspars are either surrounded by bright luminescing, non-ferroan, pore filling calcite (plate 3.3 and plate 3.6), or pyrite (plate 3.8). Vertebrate derived phosphate is also present (which is locally zoned and contains disseminated pyrite (plate 3.21 and plate 3.22), it too is surrounded by pore filling non-ferroan calcite and pyrite (plate 3.5, plate 3.21 and plate 3.22).

Plate 3.21. Calcareous sandstone, BSEM. micrograph.
Sand grade quartz (Q), K feldspar (K) and Phosphate (Ph) in calcite matrix (Ca) from Penarth 5. Qualitative EDS. analysis of the phosphate grain at a and b, showed the former point to be iron enriched.

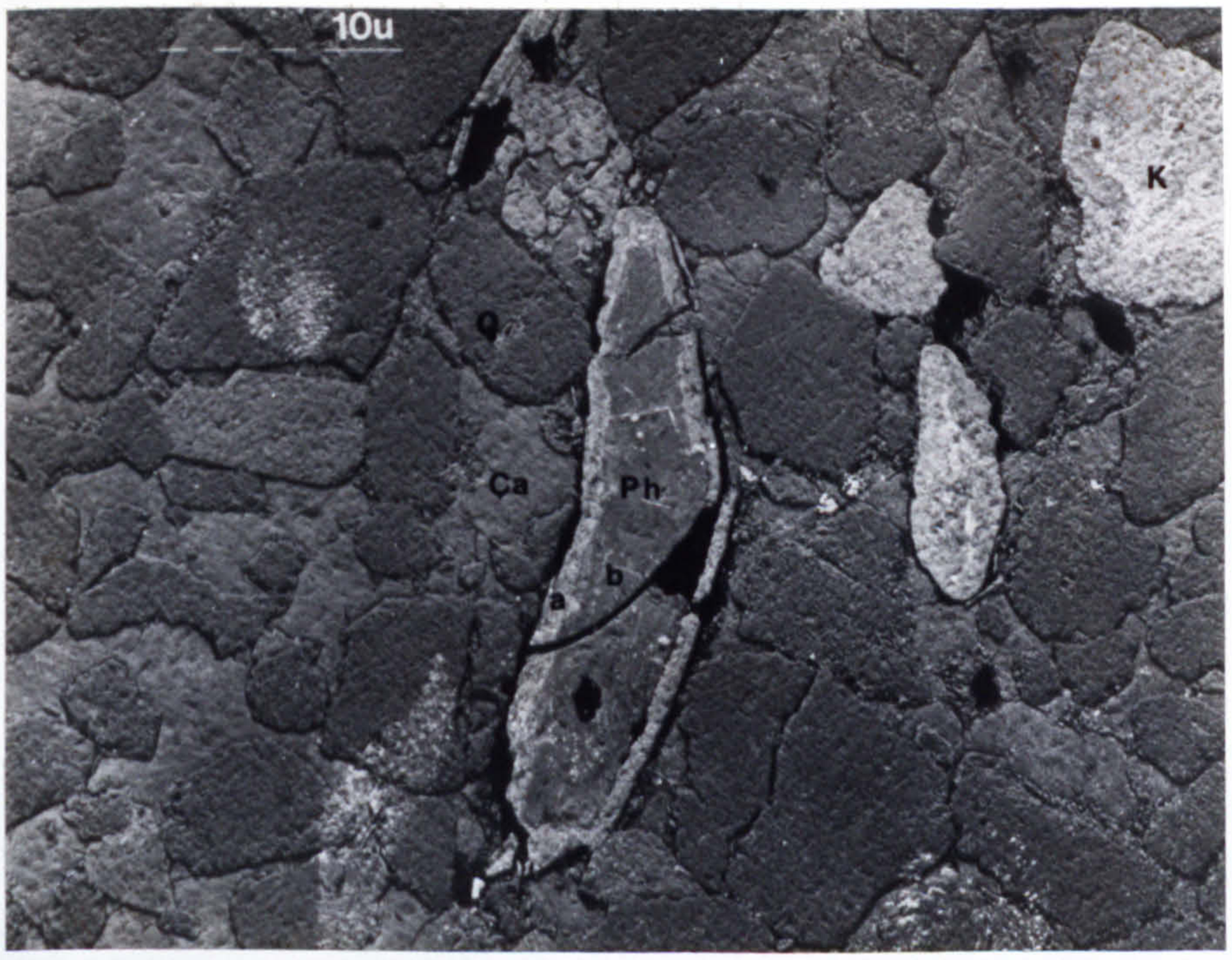
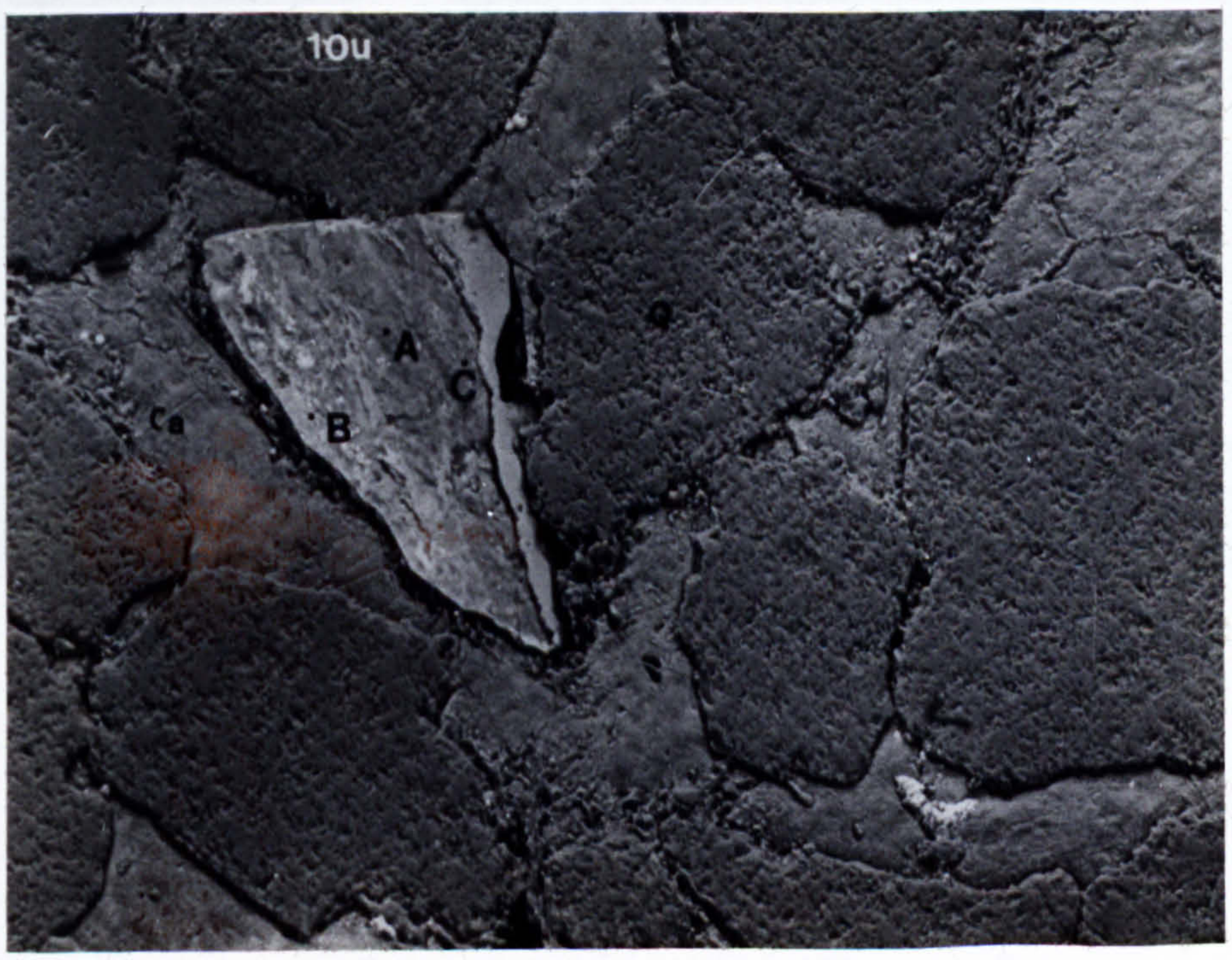


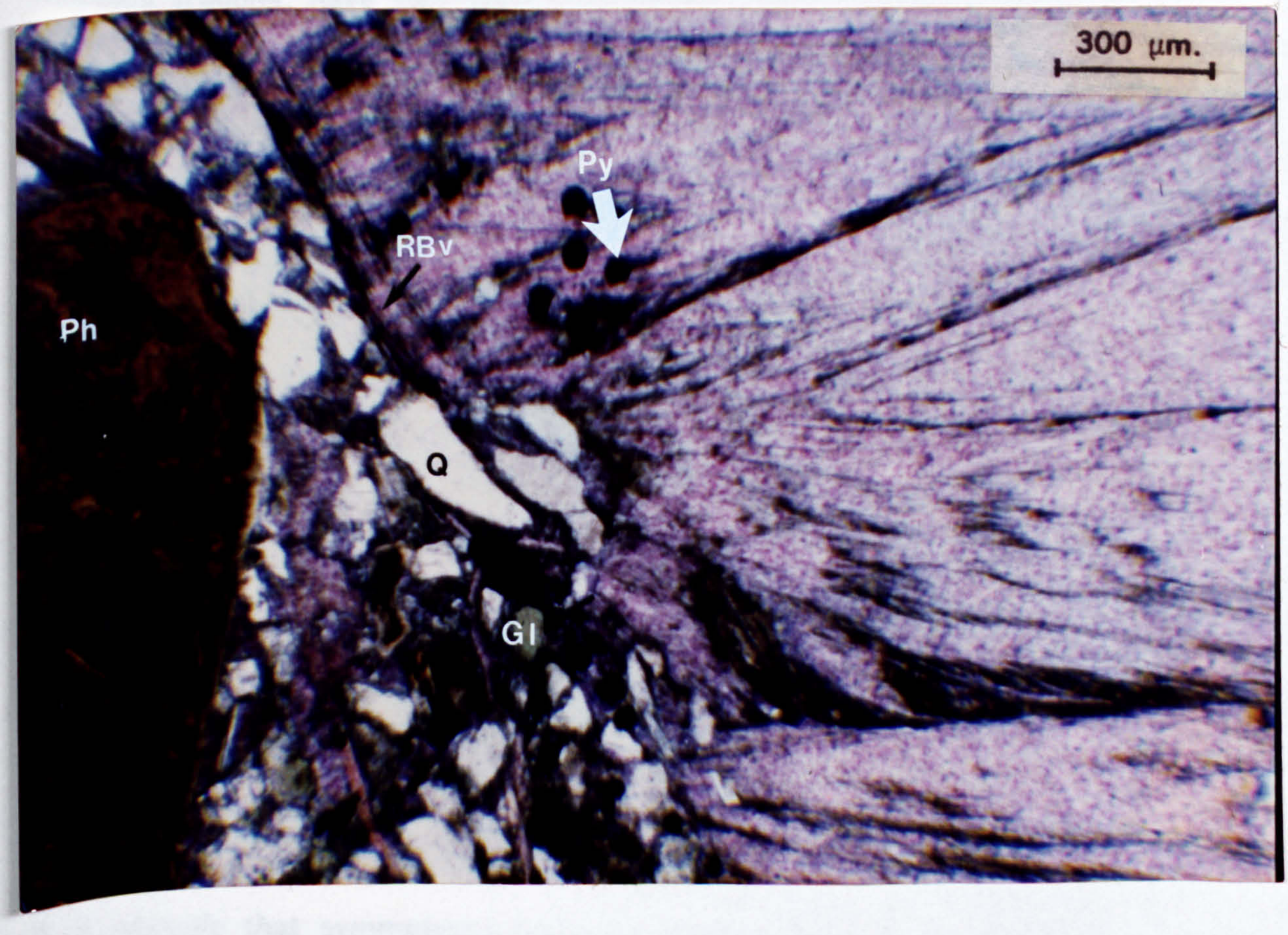
Plate 3.22. Calcareous sandstone BSEM. micrograph.
Sand grade quartz (Q) and phosphate (A,B,C) in a calcite matrix (Ca), from Penarth 5. Qualitative EDS. analysis of points A,B and C showed that B was associated with pyrite.



Within the calcareous sandstone units many of the bivalve fragments have irregular, etched margins (arrowed) (plate 3.3).

At some horizons cone-in-cone, non-ferroan fibrous vein displacive calcites (with rare included pyrite grains) overgrow the entire unit (plate 3.23). Where cone-in-cone calcites are present the bivalves exhibit pseudopleochroic textures (plate 3.23).

Plate 3.23. Cone-in-cone fabrics.
Cone-in-cone calcite overgrowing calcareous sandstone microfacies, from St. Audrie's Bay 7. The horizon contains quartz, phosphate (Ph) and glauconite pellets (Gl) in a non-ferroan calcite matrix. The cone-in-cone calcite is "seeded" upon recrystallized bivalve fragments (RBv). The cone-in-cone calcite is composed of non-ferroan calcite and contains pyrite framboids (arrowed Py).



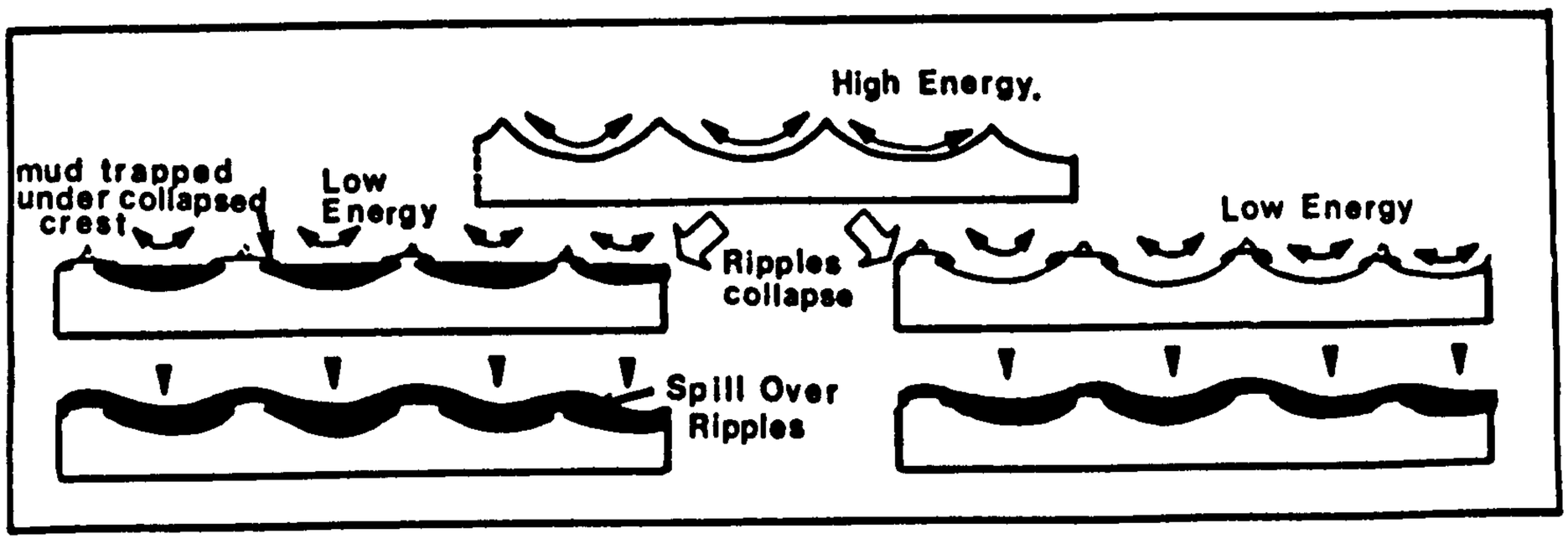
Section 3.2b. Facies interpretation.

In a sequence dominated by anoxic mud and fine silt deposits, the presence of bioturbated, intermittent, fine sandy units, both as thin continuous horizons and as starved ripples, suggests short periods of higher energy, set against background, low energy conditions, during which the sediment was oxidized. The presence of symmetrical ripples within these sandy units, further suggests that higher "energy "deposition occurred under oscillating flow conditions, either as a result of tidal activity (where both the ebb and flood tidal ellipses were of similar strength) or wave activity. In the context of the Westbury Formation wave activity is considered the more likely mechanism as the ripples are symmetrical, have sharp crests, rounded troughs, have tool marks about their crests and occasionally bifurcate (interpretation after Reineck and Singh 1980).

Wave activity alone does not explain the sudden input of oxygen and sand grade detritus into the basin. Current activity under "normal", basin bottom water conditions (i.e. anoxia) did not significantly rework the sediment nor carry in sand; thus extraordinary conditions must have occured to carry in the coarser detritus and oxygenate the sediment. However as there is no evidence of unidirectional currents it is not immediately obvious what this mechanism was. In modern shelf seas however, storm generated rip currents are a very effective mechanism for moving coarse debris offshore into deeper parts of a basin (Kresia 1981), however rip currents normally produce asymmetric bedforms (Kresia 1981). As asymmetric bedforms are not preserved (see preceding paragraph) it is only possible to tentatively postulate rip currents as the transporting mechanism (of course it is possible that symmetrical bedforms were reworked by subsequent wave activity), however as there is other evidence of storm activity (see below) rip current activity remains a strong contender as a transporting mechanism for the coarser debris.

The symmetrical ripples with reworked, rounded crests are interpreted as being spill over ripples (Seilacher 1982). Seilacher argued that spill over ripples formed during storms as a result of storm wave activity overheightening the ripple crests during peak flow conditions and subsequently reworking the ripple crests during waning flow conditions (figure 3.3 after Seilacher 1982). Hence spill over ripples are interpreted as being a direct indicator of storm wave activity.

Figure 3.3. A model for spill-over ripple formation (after Seilacher 1982). Initially the ripples are overheightened during storm surge conditions (1), as the storm subsides the ripple crests are reworked (2), mud may partially drape the crest, and the ripples take-on their characteristic terraced spill-over shape (3).



As a caveat to this last point however, Hamilton (Hamilton pers. comm. 1984) interpreted these reworked ripples as being attributable to sub-aerial drainage processes reworking wave ripples on tidal flats. In this context however this argument is rejected, as there is no collaboratory evidence of sub-aerial exposure e.g. sun cracks, rain drop impressions, vadose cements etc.

Storm events are also interpreted as having formed the elongate, semi-circular, sand-filled scour structures in the Westbury Formation. These sand filled scours are interpreted as being gutter casts (after Whittaker 1972, Goldring and Aigner 1982, Aigner and Futterer 1982 and Greensmith *et al.* 1980). Gutter casts are believed to form where storm generated, helical flow impinges on the sediment and gouges out elongate, gutter shaped grooves with helical striae on their sides. This scouring is followed by sand fill during waining flow conditions (Whittaker 1972 and Goldring and Aigner 1982).

In the context of the Westbury Formation gutters, the storm scours were initially filled with reworked, convex up bivalves and then by sand. The sand infill contains only horizontal laminae and no transition flow laminae (figure 3.2). Thus, using modern sediments as an analogue (Reineck and Singh 1980) it is likely that the infill occured in subaqueous, low energy conditions, where a potentially fabric-destructive infauna was absent as a consequence of overall sediment anoxia. (It is of course conceivable that sand fill could have occurred in upper flow regime conditions. However this is considered unlikely as there are no transitional flow laminae.)

In some units the base of the *Thalassanoides sp.* burrows are scalloped, their tops partially eroded and in general they are poorly defined. They are similar to "tiered burrow" structures described by Seilacher (1982), where he suggested that storm generated wave scour had modified the original burrow morphology in relatively shallow water.

Diagenesis.

The presence of trace fossils (e.g. *Thalassanoides sp.*, *Pelecypodichnus sp.* and Limulid resting traces) indicates that the bottom water and the top few centimetres of the sediment were oxygenated, at least for a short period after the storm events (with the exception of deposition after the gutters, see above) and that hydrogen sulphide concentrations were initially fairly low (as hydrogen sulphide is toxic to most macro-organisms). The respiration of this aerobic macrofauna community may have caused the pore water acidity

to increase (as a byproduct of carbon dioxide production) and may be the mechanism reponsible for the early etching (pre-cement precipitation) of the shell debris.

Interestingly the Westbury Formation calcareous sandstones, also locally contain significant quantities of zoned, vertebrate derived phosphatic debris. In normal oxic conditions in modern sediments, hydroxyapatite (bone) and phospholipids are destroyed by scavenging animals and bacteria, and the phosphate is recycled back into the ecosystem (Schafer 1972, Froelich *et al.* 1979). The preservation of phosphate in the Westbury Formation thus implies that this recycling process failed; and that the calcareous sandstones acted as a phosphate sink. The most obvious reason for this, using modern analogues as a comparison, is that anoxia was re-established in the sediment fairly soon after deposition (possibly as a result of opportunistic macrofaunal colonization after a storm), thereby limiting long term colonization and phosphate recycling (Trudinger 1976, Riggs 1979 and Bremner 1980); a point reinforced by the presence of disseminated pyrite associated with the phosphate (see below). In addition to the bone being preferentially preserved the presence of zoned phosphates indicate that inorganic phosphate was also precipitated on to the organic nuclei, which suggests that the early pore waters were in disequilibrium with calcite and that phosphate and bicarbonate ions were in solution. This implies that the pore waters were in the phosphate rather than calcite stability field - i.e. at pH's between 7 - 7.8 (Krumbein and Garrels 1952) slightly lower than normal marine conditions (Drever 1982).

The presence of euhedral, K feldspar overgrowths on bright luminescing, etched K feldspar cores prior to calcite cement precipitation indicates that following early acidic conditions (associated with aerobic respiratory processes) and K feldspar etching the pore waters quickly became alkaline and supersaturated with respect to potassium, aluminium and silicon ions (Kastner 1971, Ali and Turner 1982). This shift in pore water conditions caused the precipitation of K feldspar overgrowths on the etched high temperature detrital K feldspar cores. (n.b. The cores are interpreted as having a high

temperature, detrital origin as they luminesce bright blue and are thus probably rich in titanium (Nickel 1978), and cannot be authigenic as the Westbury Formation has not been through the oil generation window (section 3.6b) in contrast to the dull luminescing authigenic overgrowths.

The component ions for this authigenic K feldspar phase almost certainly derive from the dissolution of other detrital silicates e.g. illite and kaolinite. K feldspar, illite and kaolinite form part of an equilibrium series (Longstaffe 1981) with K feldspar being in equilibrium at the highest pH's. As detrital illites and kaolinites are present in the clay fraction their partial dissolution during early diagenesis may well have provided the necessary ions for K feldspar precipitation. Further as the K feldspar overgrowths are not etched it is probable that once the pore waters became alkaline the pH never dropped out of the K feldspar equilibrium field.

An obvious cause of this early pH switch may have been the onset of overall sediment anoxia and the development of reducing conditions as a result of the return to low energy deposition and oxygen demand exceeding oxygen supply. This suggestion is backed up by pyrite being present as a pore filling phase often surrounding and in intimate association with the K feldspars, it is worth noting however that there is no evidence of pyritic inclusions within the overgrowths.

Following the precipitation of the K feldspar overgrowths pyrite and non-ferroan calcite cements infilled the porosity. Pyrite only forms in modern sediments in anoxic conditions with low redox potentials, where bacterially mediated sulphate reduction is supplying dissolved sulphides to the pore waters (Berner 1970). The dissolved sulphides react with dissolved Fe^{++} (which is itself derived from the reduction of detrital iron oxides Curtis 1980) via a series of intermediates to form pyrite (Berner 1984). Iron reduction increases the pore water alkalinity (Curtis 1980) and this coupled with the increased bicarbonate concentrations (as a result of the bacterial oxidation of organic matter) causes the local precipitation of non-ferroan calcite

cements associated with the precipitation of pyrite (Curtis 1977); it is worth noting that where both reduced sulphides and Fe(II) are present pyrite always forms in preference to ferroan calcites (Garrels and Christ 1965).

As the sulphate is derived by diffusion downwards from the water column (Curtis 1980), then the non-ferroan calcite and pyrite cements, and by necessity the K feldspar overgrowths must be very early cement phases (forming within a few metres of the sediment water interface). As iron and sulphate reduction are the proposed mechanisms for controlling both, the pore water alkalinity for K feldspar overgrowth formation and the precipitation of pyrite and associated non-ferroan calcites, it is interesting to speculate why K feldspars are always an earlier precipitation phase than either calcite or pyrite. As there is no obvious mechanism for controlling this relationship it is presumably due to the relative availability of the precursor ions for these different phases, with K^+, Al^{+++} and SiO_2 being made available earlier than Fe(II), HS^- or HCO_3^-. With a potential mechanism for this being the early dissolution of the metastable clays on account of their large surface area. It is worth noting that the quartz grains are not etched, which suggests that the pH never rose much above 9. Thus pHs during the early diagenetic phase probably never went much below 7 or above 9.

Texturally the last diagenetic phases to form were the fibrous non-ferroan cone-in-cone calcites, which overgrow some of the calcareous sandstone units. Where these fibrous calcites are present recrystallization and local dissolution has been intense and the originally aragonitic bivalve debris has recrystallized to non-ferroan calcite and produced pseudopleochroic textures. Consequently it is likely that at least some of the ions for this late stage fibrous calcite growth were derived from the dissolution of bivalve debris (a similar source has been postulated by Marshall (1981) for Lower Jurassic fibrous calcites from Southern England). The bicarbonate ions for this process are almost certainly derived from the oxidation of organic matter. The main problem identified in this process is however to determine exactly when these cone-in-cone calcites formed? Some of the Westbury Formation

cone-in-cone calcites contain included framboids which indicates that they formed either: during the latter part of sulphate reduction, during methanogenesis or thermal decarboxylation. The fibrous calcites in the Westbury Formation are composed of non-ferroan dull luminescing calcite which suggests that free iron was not available for incorporation into the growing crystal lattice. This indicates either deposition in the oxic zone, which in this context is obviously naive, or post iron reduction in an iron limiting environment (i.e. during the methanogenic or thermal decarboxylation zones) with either of the latter the more probable scenario. The presence of the pyrite framboids are due to them being accidentally incorporated into the growing crystal.

This dissolution process associated with cone-in-cone formation suggests that the pore water pH's may have also been lowered during cone-in-cone emplacement. Processes lowering the pH during methanogenic and thermal decarboxylation have been reviewed by a number of authors e.g. Carothers and Kharaka (organic acid production, Carothers and Kharaka 1978), Boles and Franks (illite/smectite to illite transformation, Boles and Franks 1979) and Curtis (thermal decarboxylation, Curtis 1980). Despite these constraints however the precise depth at which these fibrous calcites formed is unknown.

A summary of the diagenetic processes within the calcareous sandstones is presented in figure 3.4.

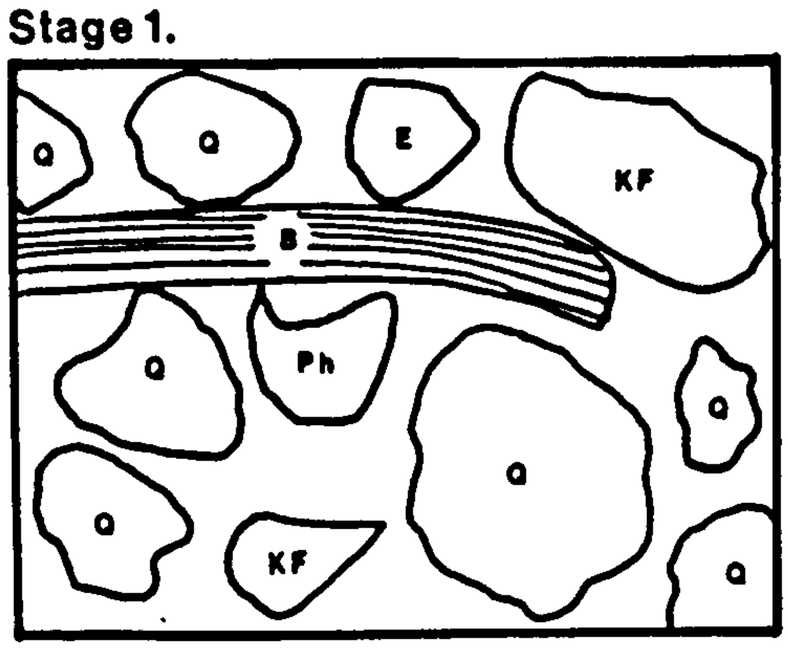
Figure 3.4.

Stage 1, Marine phreatic. Deposition of sand grade quartz, K feldspar, calcitic and phosphatic debris.

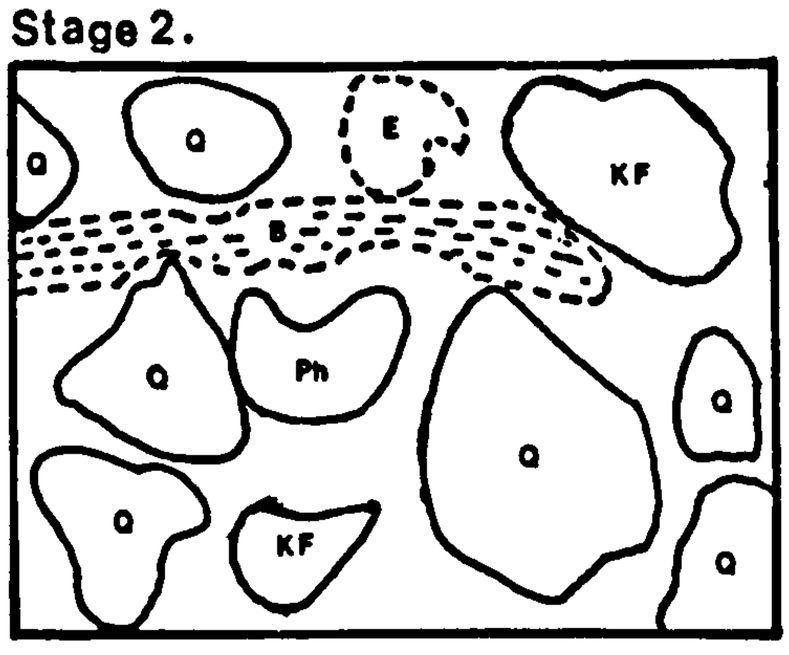
Stage 2, Early diagenesis, aerobic zone. Early compaction of the detrital components, with etching of the calcitic material, as a possible consequence of the development of acidic pore waters as a result of aerobic respiratory processes.

Stage 3, Deeper diagenesis within the anaerobic zone, sulphate reduction to early thermal decarboxylation. Shift to alkaline pore water, as a result of iron reduction causes the precipitation of K feldspar and phosphatic cements on pre-existing nuclei, followed either by non-ferroan calcite or pyrite precipitation in the pore spaces (depending on the local concentration of the component ions). Finally non-ferroan calcite cone-in-cone formation occurs in iron limiting pore waters, within either the methanogenic or thermal de-carboxyaltion zones.

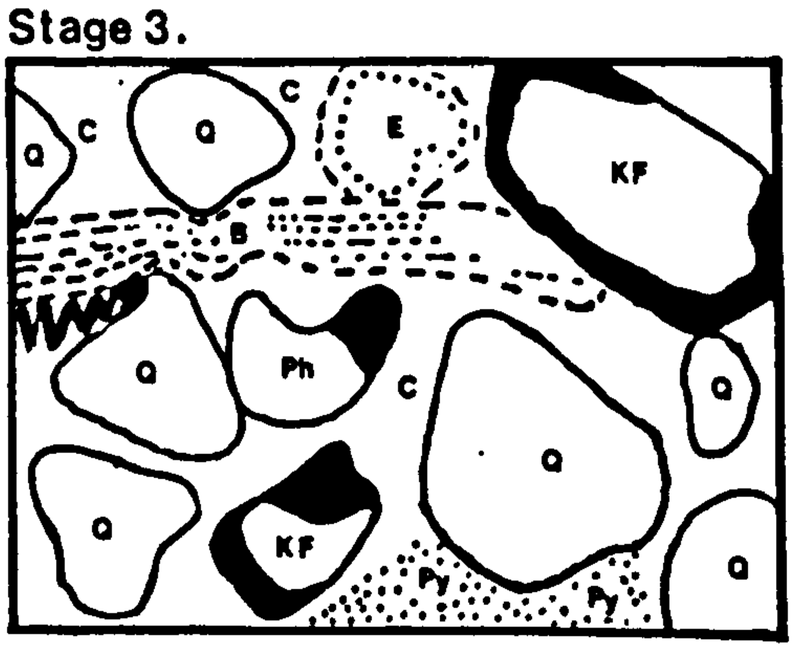
Stage 1.



Stage 2.



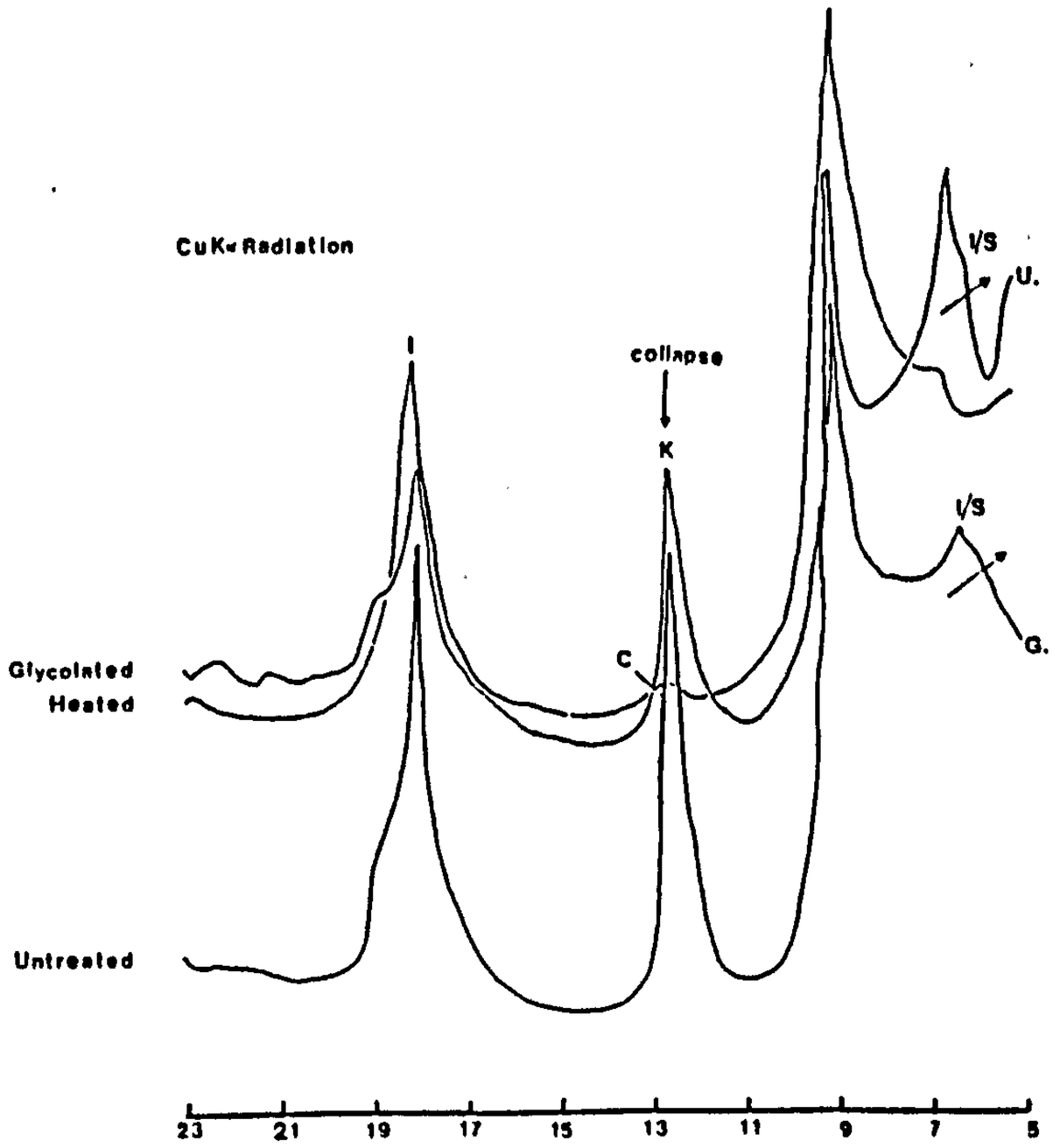
Stage 3.



Section 3.3a. Calcarenaceous sandstones.

The calcarenaceous sandstones in the Westbury Formation are mainly composed of fine sand grade quartz (plate 3.24), reworked calcareous biogenic debris (plate 3.25), minor amounts (<5%) of K feldspar (with overgrowths) (plate 3.26), and clay grade illite, kaolinite and "mixed layer" illite/smectite. (figure 3.5). Locally however the calcarenaceous sandstones contain reworked cobbles from the underlying units (plate 3.27) (which are usually dolomitic and exhibit de-dolomite textures, plate 3.28) and significant quantities of detrital phosphate (francolite, figure 2.2) (e.g plate 3.29 and plate 3.30). At one locality algal lamination is present (plate 3.31).

Figure 3.5. X-Ray spectra of the untreated, glycolated and heated <2um. fraction from Westbury 5 (calcarenaceous sandstone facies). The dominant clays are illite (I), "illite/smectite" (I/S) and kaolinite (K). Glycolation has caused the expansion of the illite/smectite "mixed layer" phase, and heating to 550°C. has caused the kaolinite peak to collapse.



The main pore filling mineral, within these calcarenaceous sandstones is non-ferroan (e.g. plate 3.24, plate 3.25 and plate 3.29), bright luminescing calcite (e.g. plate 3.26, plate 3.28 and plate 3.30) with subsidary amounts of pyrite (plate 3.25).

Texturally the pore filling calcite comprises recrystallized sparry calcites (plate 3.25 and plate 3.32), in which there are remnant micrite patches (plate 3.33) and many of the allochemical components appear to float (e.g. plate 3.25). Most of the bivalve fragments exhibit pseudopleochroic textures (plate 3.25, plate 3.33) and are composed of non-ferroan, bright luminescing calcite (plate 3.28); however some have been completely replaced by sparry calcite and are now only visible as a consequence of the presence of remnant micrite envelopes (plate 3.34 and plate 3.36), whilst others have been replaced by pyrite (plate 3.35).

The calcarenaceous sands rest disconformably on the underlying facies and are unbioturbated. Interbedded, stacked, fining upward microfacies couplets are preserved (plate 3.27) which comprise:- calcareous sandstone and calcarenaceous sandstones, calcarenaceous sandstone and bioclastic wackestones (plate 3.32, plate 3.37), and conglomeratic units and calcarenaceous sandstones (plate 3.27). Within these couplets the sediment of the finer, overlying unit often partially infiltrates the top few mm. of the underlying packet (plate 3.32). The couplets are separated from one another by erosion surfaces (plate 3.27).

The bivalve debris has been reworked and is mainly preserved, disarticulated and convex-up (3.27), although occasionally end-on fabrics are observed (plate 3.27).

Plate 3.24. Calcarenaceous sandstone (p.p.l.).
Sand grade quartz (Q), recrystallized bivalves (Bv) and minor amounts of phosphatic debris in a matrix of non-ferroan calcite (NFC) micro- (M) and pseudospar, from Sedbury 3. The bivalves have recrystallized and preserve no internal structure.

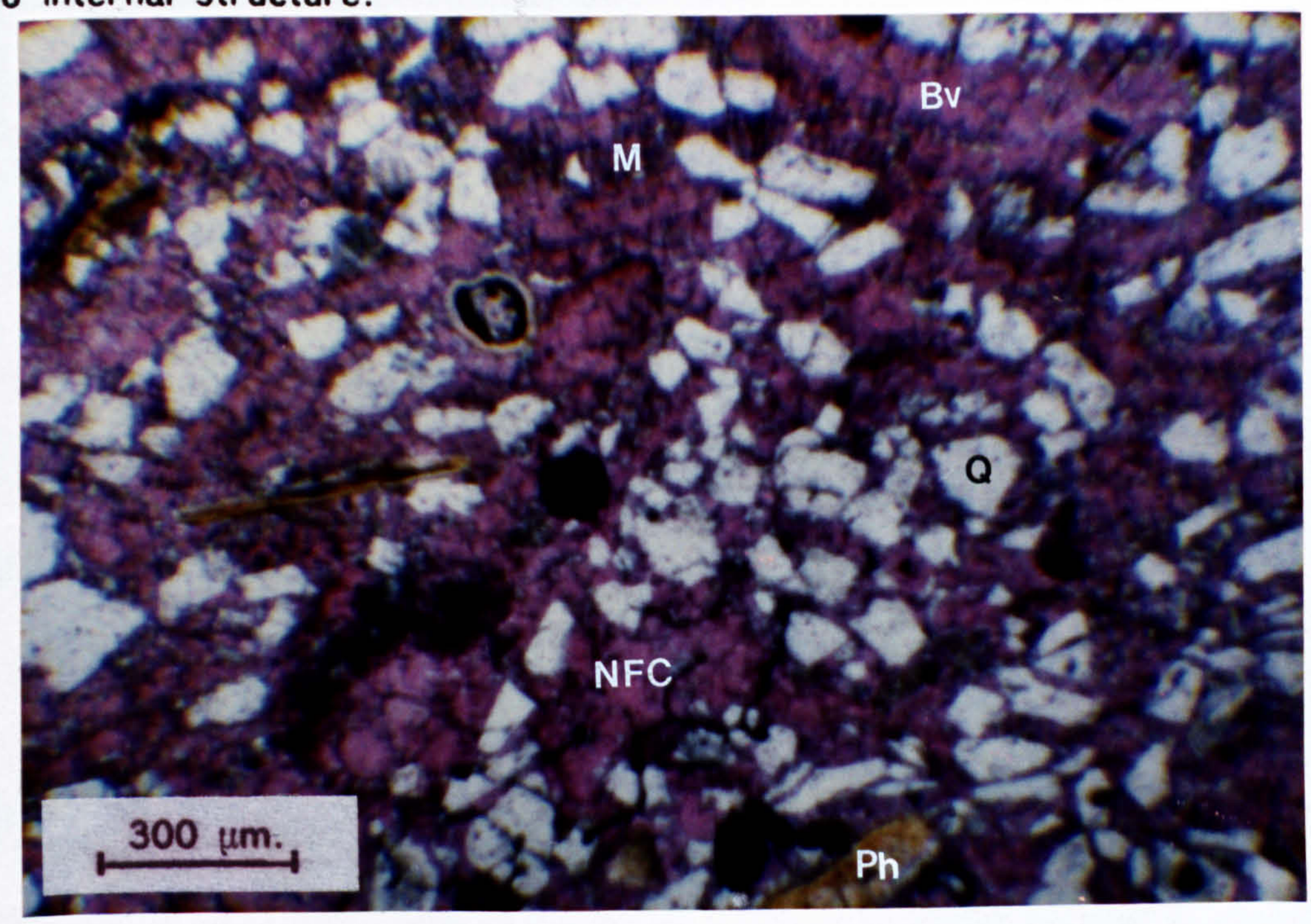


Plate 3.25. Recrystallized shell debris in calcarenaceous sandstone (p.p.l.).
Medium grade quartz sand (Q), phosphatic debris (Ph) and recrystallized bivalves (RBv) in a non-ferroan calcite pseudospar (NFC), from Carrefour 8. The bivalves exhibit pseudopleochroic textures (arrowed) and are in optical continuity with the pseudospar. Locally pyrite replaces the calcite (Py).

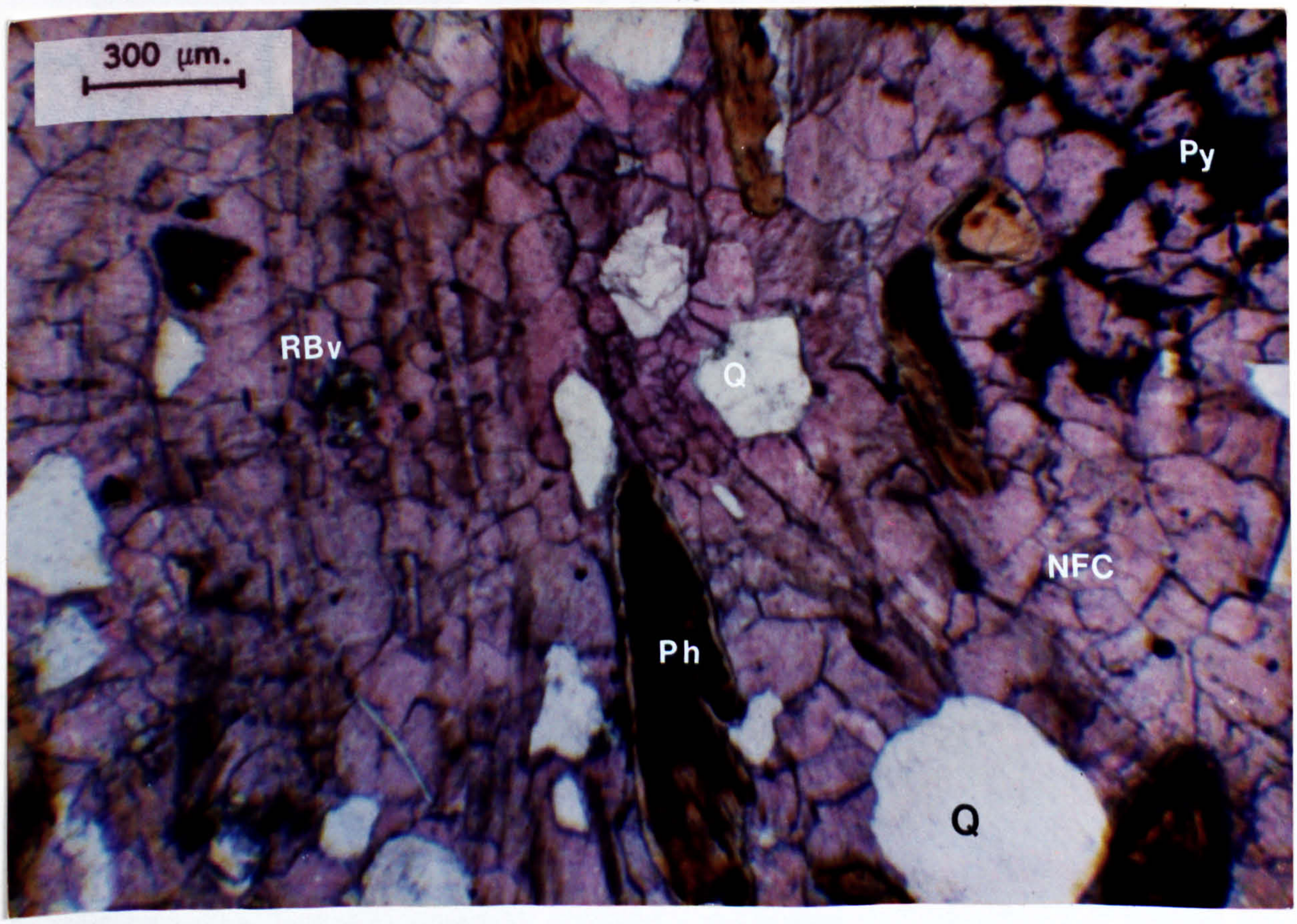


Plate 3.26. Calcarenaceous sandstone (CL.).
Phosphate (Ph), quartz (Q) and K feldspar in a bright luminescing, unzoned non-ferroan (NFC) calcite matrix from Westbury 5. The K feldspar grains have well deveoped euhedral overgrowths.

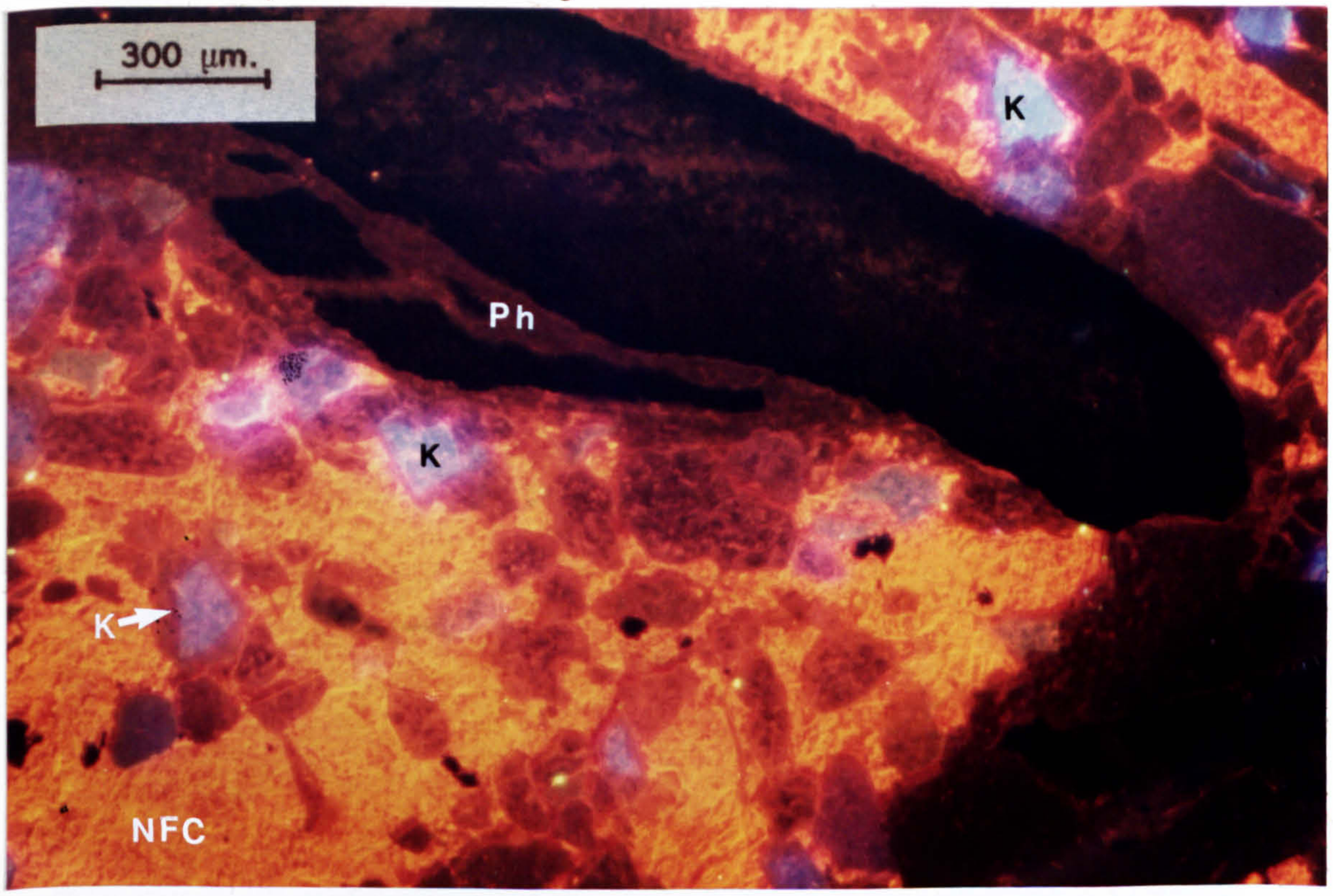


Plate 3.27. Sediment packets.
Three partially preserved superimposed fining upward, sediment packets, from Watchet Harbour 9. Comprising a disarticulated shell and phosphatic lag at their base (with conglomeratic clasts in cycle 3) overlying an erosion surface (arrowed E), fining upward into a wackestone. It is worth noting that the cycles are not always complete with for instance the mudstone part of cycle 2 being truncated by the coarse lag of cycle 3. The bivalves in the shell lag tend to be preserved convex-up although some are supported in an apparently unstable position end-on (arrowed).

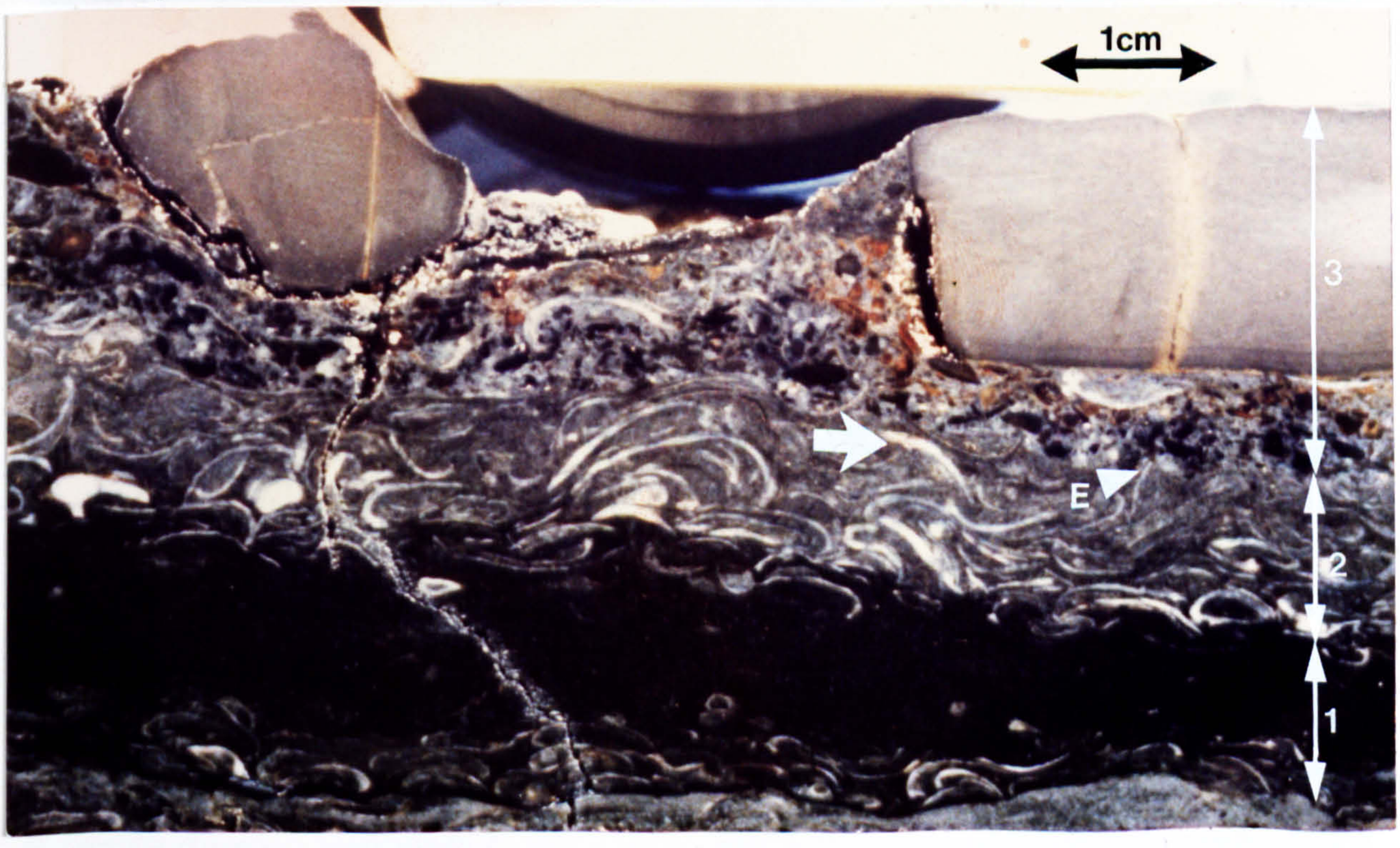


Plate 3.28. Calcarenaceous sandstone, with de-dolomite and phosphate clasts in bright luminescing calcite (CL.).
Phosphatic debris (Ph), detrital K feldspar grains (K), dolomite clasts (DeD) and quartz in a bright luminescing (NFC) calcite matrix, from Carrefour 7. The detrital dolomite clasts are inverting to non-ferroan calcite forming a de-dolomite texture (DeD). The K feldspars (K) have well developed early non-luminescing overgrowths. The detrital components appear to float in the calcite matrix, because the bivalves and original pore filling micrite have inverted to undifferentiated calcite pseudospar.

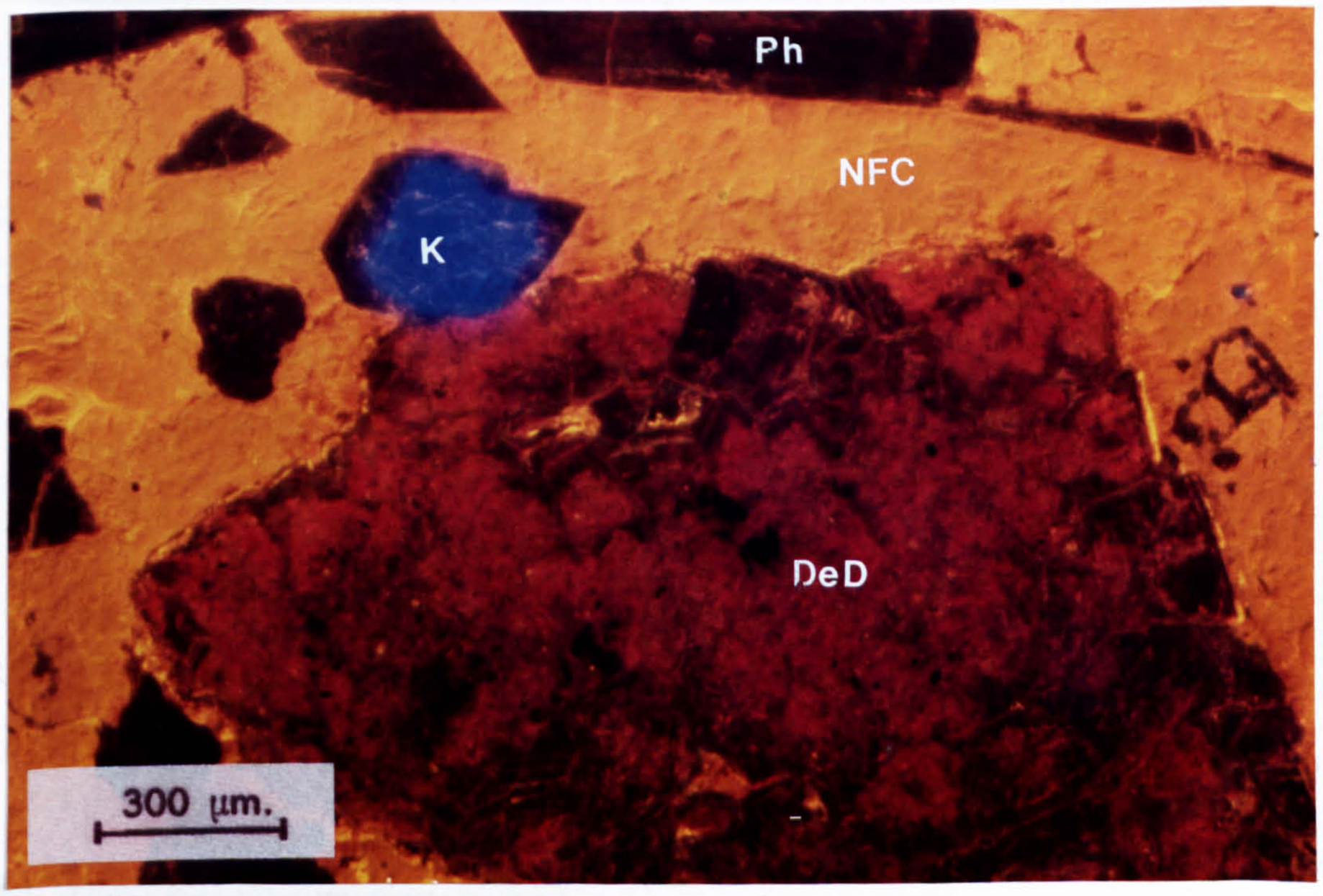


Plate 3.29. Calcarenaceous sandstone (p.p.l.).
Sand grade quartz (Q, phosphatic debris (Ph), and minor quantities of micas (arrowed M) in a non-ferroan calcite matrix (NFC), from Aust 2. The quartz is bimodal having two distinct grain sizes - fine and coarse sand. The phosphatic debris includes *Gyrolepis sp.* and indeterminate vertebrate derived material.

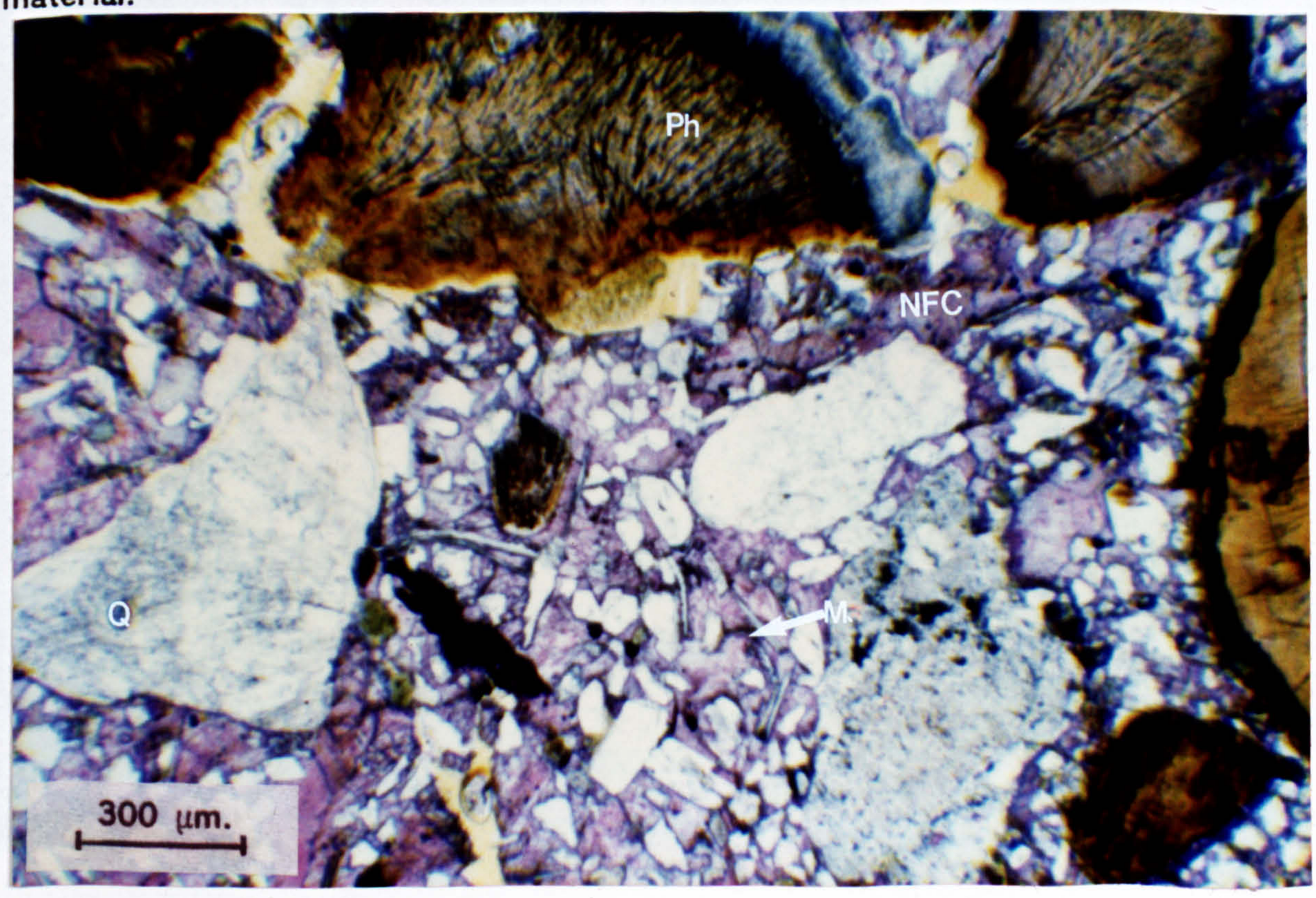
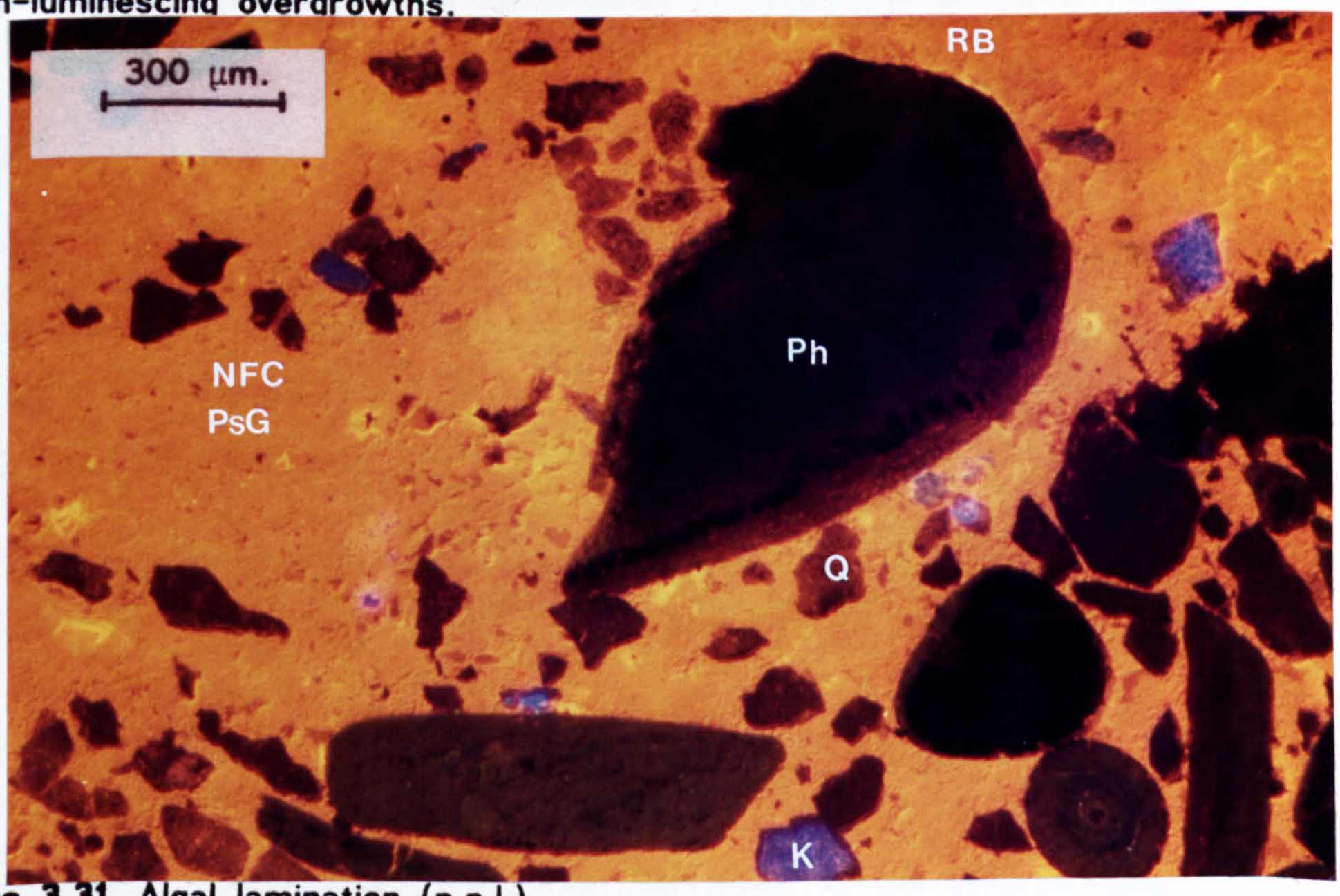


Plate 3.30. Calcarenaceous sandstone with abundant phosphatic debris (CL.). Vertebrate derived phosphatic debris (Ph), fine sand grade detrital quartz (Q) and K feldspar grains in a bright luminescing calcite matrix (NFC), from Wetmoor Wood 2. Much of the detrital debris appears to float in the matrix, because the metastable carbonate phases have recrystallized to a bright luminescing pseudograinstone (PsG). The recognisable phosphatic debris is derived from *Gyrolepis sp.* and *Birgeria sp.*, whilst the unrecognisable material is assumed to have a vertebrate origin. The detrital K feldspars (K) have non-luminescing overgrowths.



Pate 3.31. Algal lamination (p.p.l.).
Recrystallized algal filaments (arrowed A) in a calcareous microspar (M) and pseudospar (Ps) matrix with rare quartz (Q) and phosphate grains (Ph), from Aust 2.

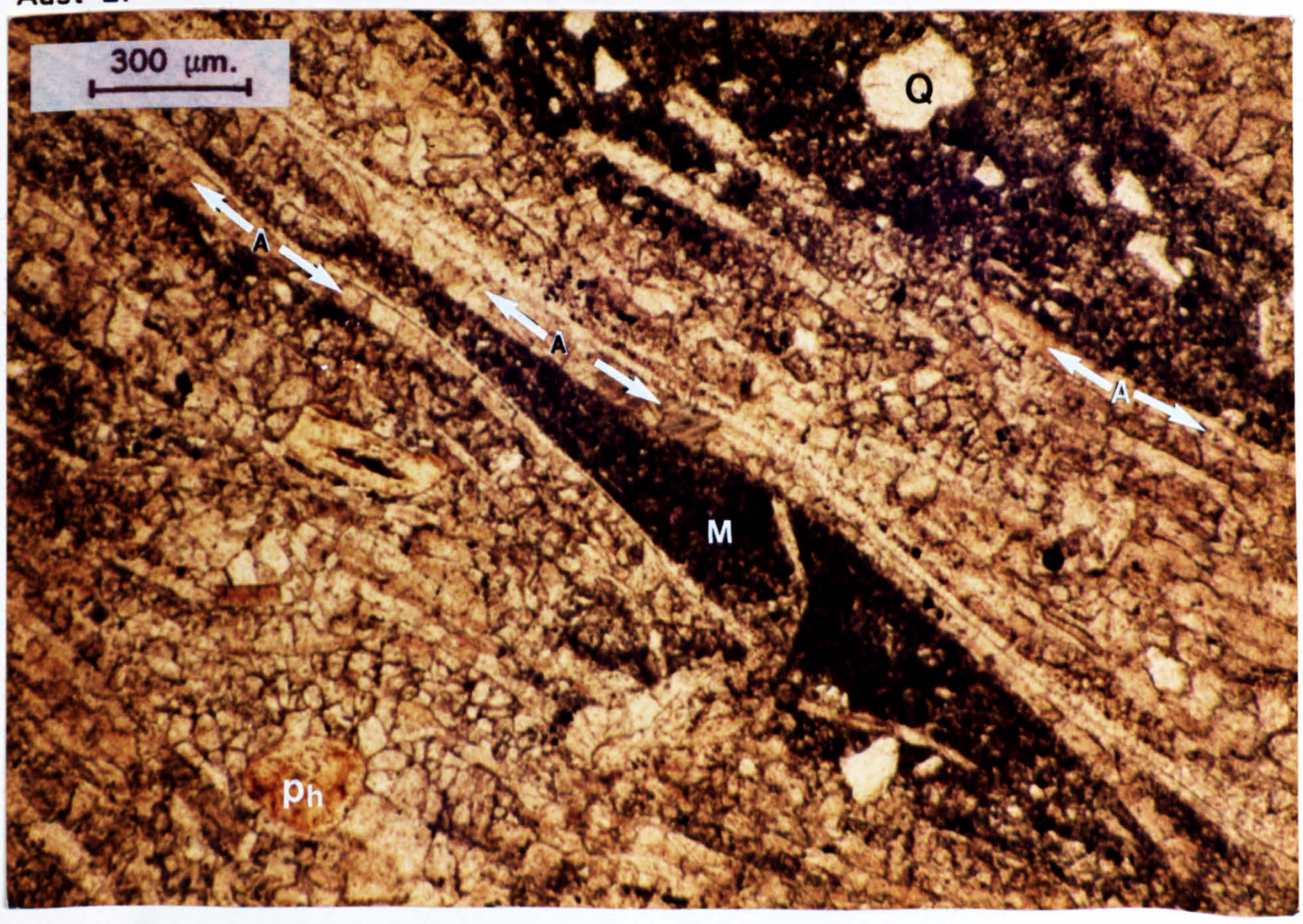


Plate 3.32. Interbedded microfacies with calcarenaceous sandstone overlain by bioclastic packstone (p.p.l.).
The basal couplet is composed of sand grade quartz (Q) in a non-ferroan calcite matrix. The matrix is composed both of micrite and sparry calcite. The upper part of the couplet is composed of recrystallized bivalves (Bv) in a non-ferroan calcite matrix, with the calcite matrix in the upper couplet being composed of micrite (M) and sparry calcite (NFC).

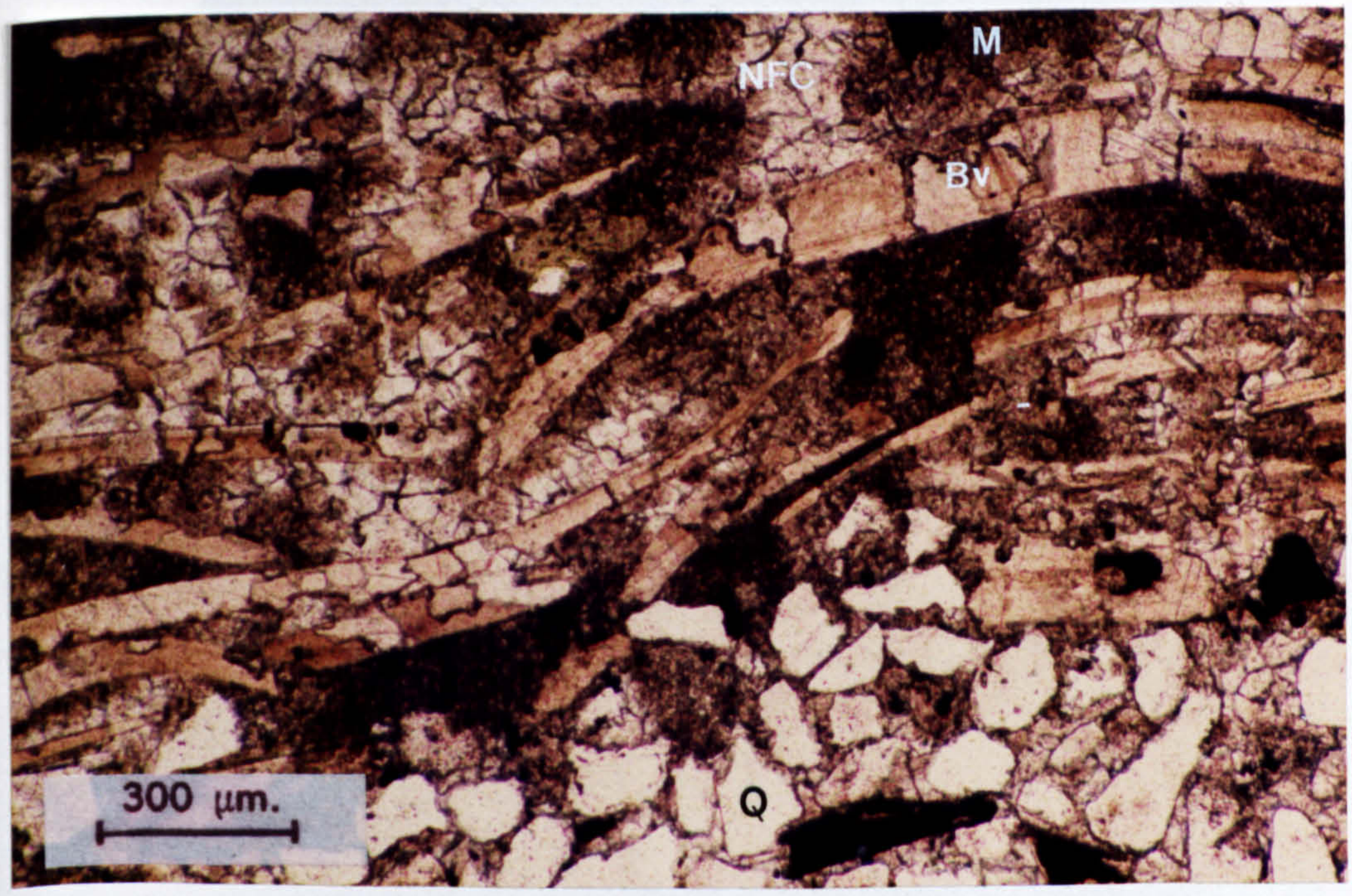


Plate 3.33. Calcarenaceous sandstone with recrystallized bivalves (p.p.l.).
Medium sand grade quartz (Q), bivalves (Bv) and phosphatic debris (Ph) in a non-ferroan calcite pseudospar, from Carrefour 8. The bivalves have recrystallized, although remnant internal lamination (Bv) is still visible. Most of the primaary pore filling calcite has recrystallized to pseudospar, although some relict micrite patches (Rm) are present. Most of the vertebrate debris is of indeterminate origin, although *Birgeria sp.* is recognisable.

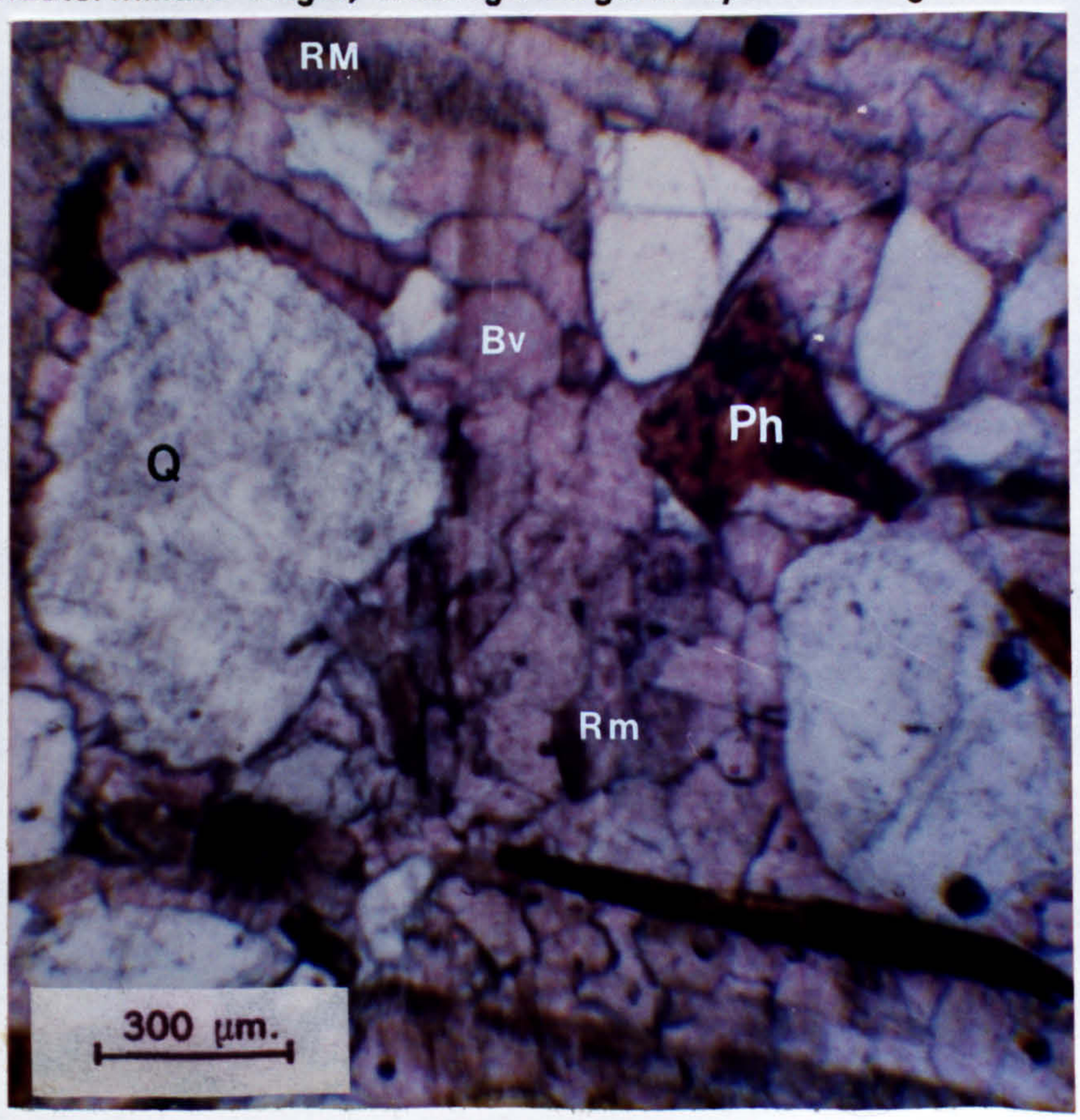


Plate 3.34. Neomorphic fabrics in calcarenaceous sandstone (p.p.l.). Sand grade quartz (Q), phosphatic debris (Ph) and recrystallized bivalves (Bv) in a matrix of non-ferroan calcite pseudospar (NFC) from Aust 2.

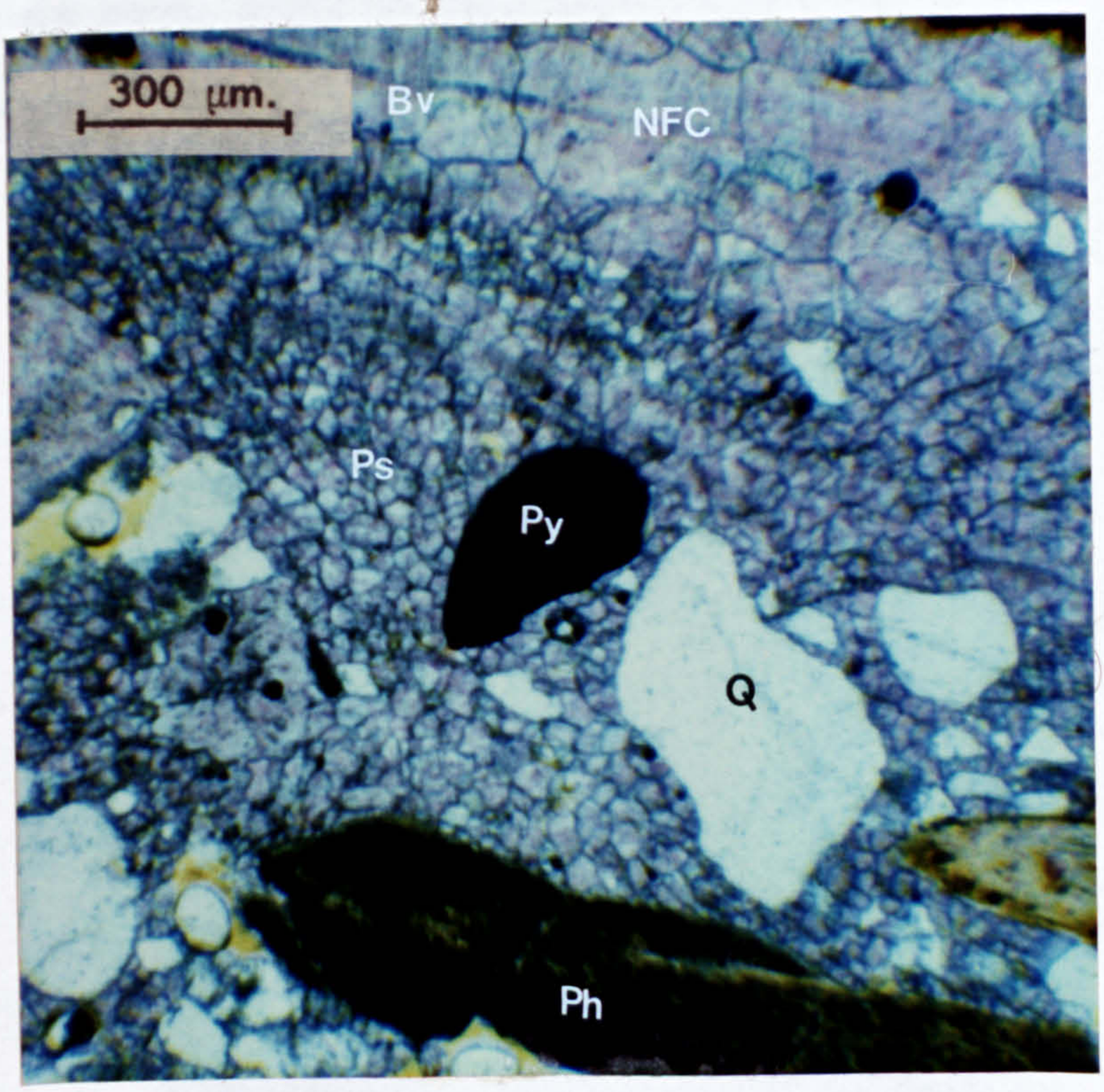


Plate 3.35. Calcarenaceous sandstone with pyritized bivalves (p.p.l.). Broken bivalves (Bv), quartz, and phosphatic debris (Ph) in a non-ferroan calcite cement, Some of the bivalve material has been completely replaced by pyrite (Py), whilst the rest has only been partially replaced.

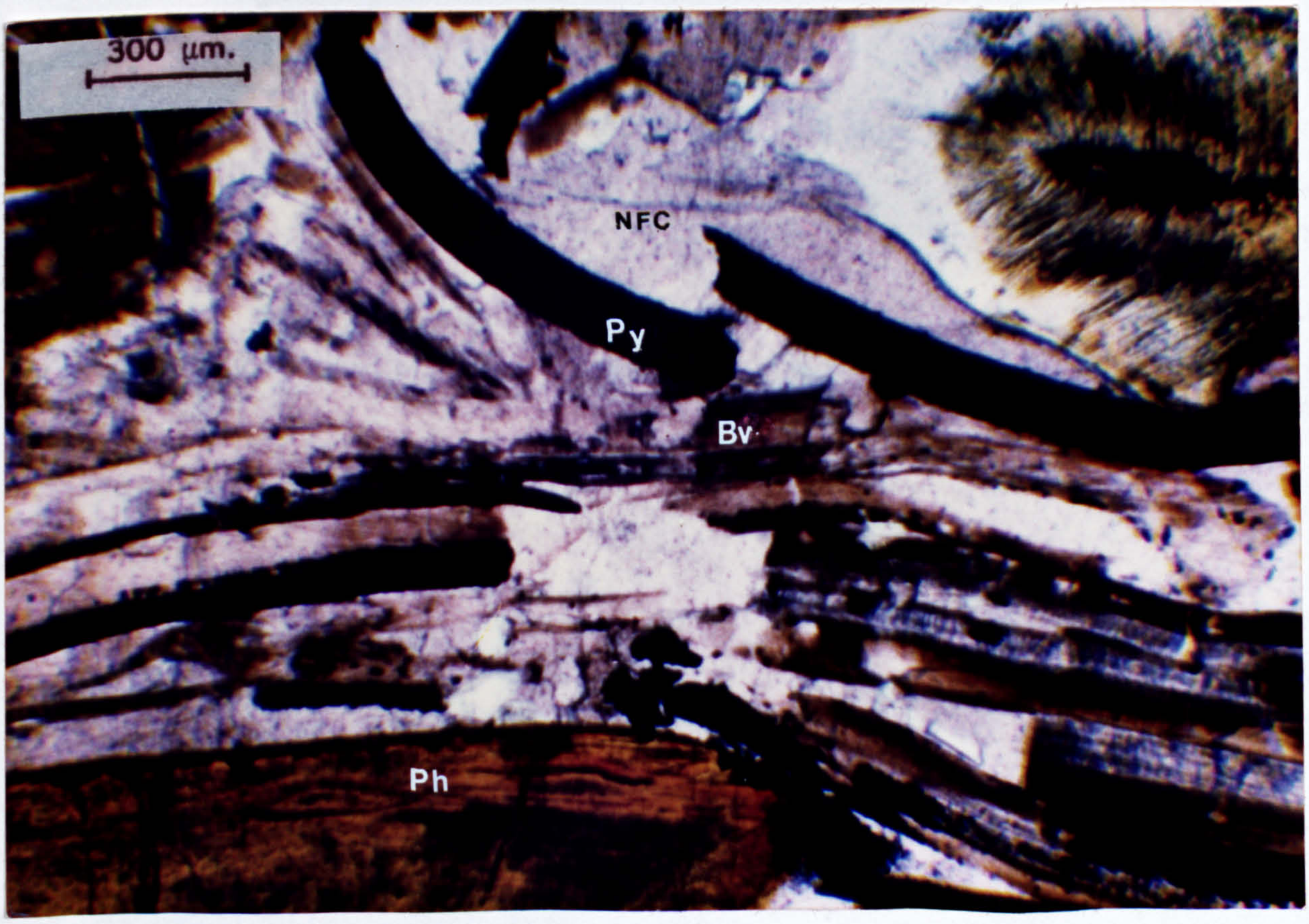


Plate 3.36. Calcarenaceous sandstone with recrystallized bivalves (p.p.l.). Sand grade quartz (Q), phosphatic debris (Ph) and recrystallized bivalves (RB) in a matrix of non-ferroan calcite (NFC), from Carrefour 8. The recrystallized bivalves are barely visible and are only revealed as a consequence of their pyritized micrite envelopes (Pm.). Locally pyrite has replaced some of the pseudospar.

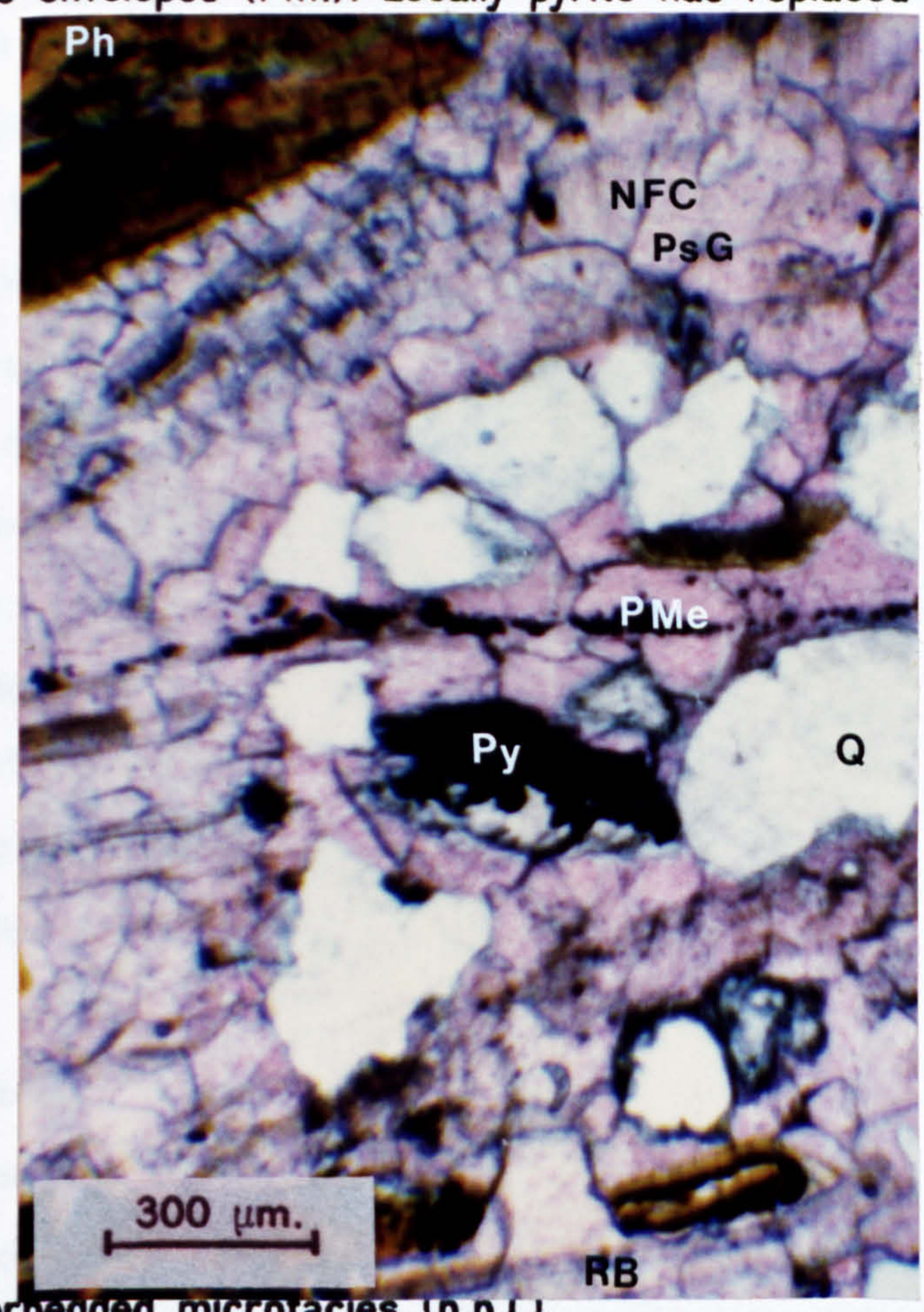
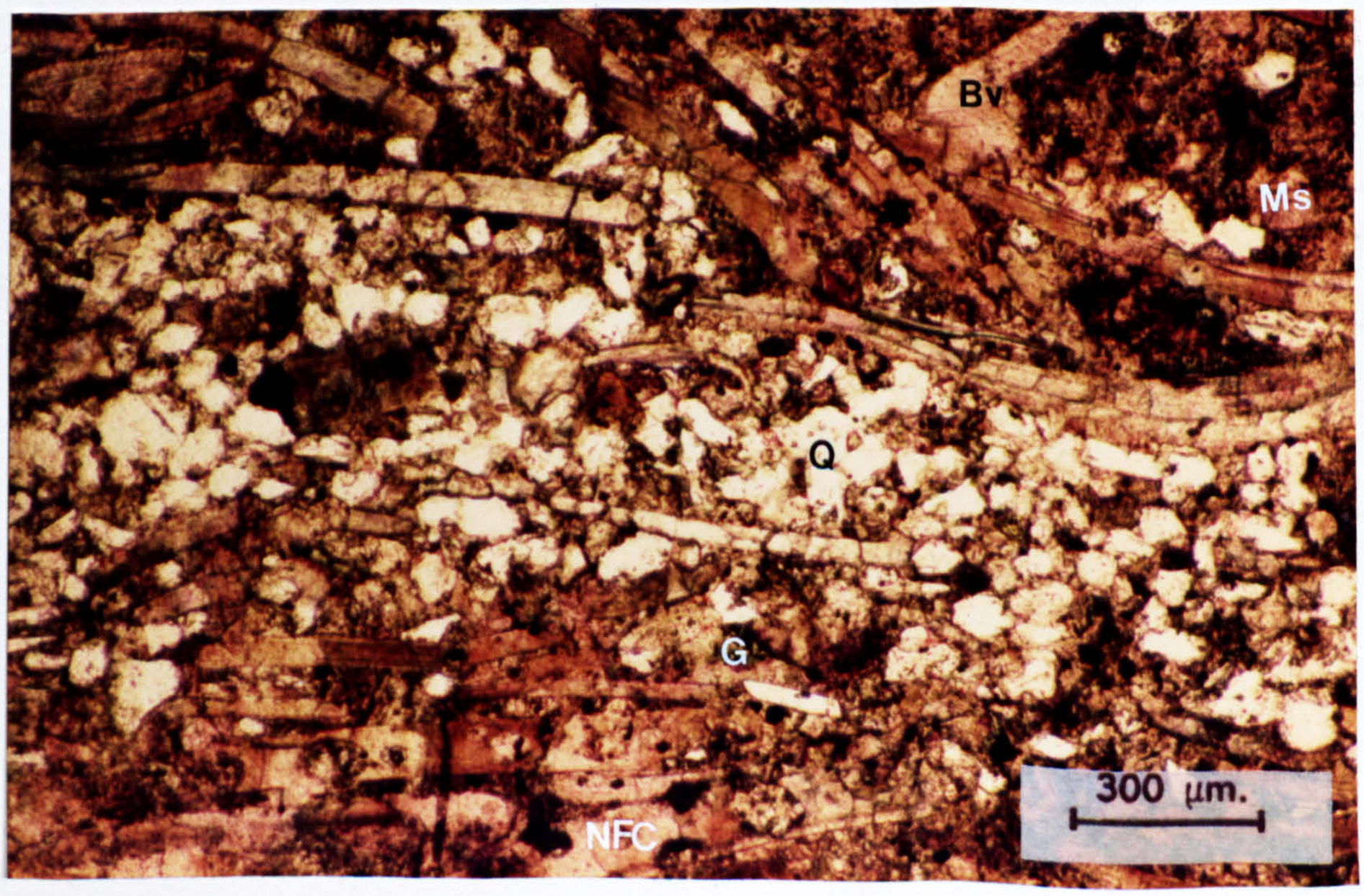


Plate 3.37. Interbedded microfacies (p.p.l.). Reworked, disarticulated, mainly convex-up bivalves (Bv), detrital sand grade quartz (Q) and glauconite pellets (G) are preserved in non-ferroan, inclusion rich calcareous spar (NFC). The bivalves have been recrystallized and now composed of non-ferroan calcite. The sand grains are concentrated into small lenses.



Section 3.3b. Facies interpretation.

The stacked fining upward sequences and facies couplets, which account for the alternating microfacies changes are interpreted as being superimposed graded rhythmites (after Reineck and Singh 1980). Graded rhythmites are believed to form where storm waves impinge on the sea floor. Initially this causes the finest sediment fractions to be placed in suspension whilst the coarser fraction is stirred-up; then as storm activity subsides the suspended fraction settles out, draping and infiltrating the underlying coarser fraction (after Reif 1982, Kresia 1981 and Kresia and Bambach 1982), to produce the characteristic graded rhythmite couplet overlying the erosion surface. The storm mixing of the coarse part of the graded rhythmite is also believed to form the end-on bivalve fabrics (Kresia 1981) and in this context may also be responsible for the reworking of the underlying sediment producing the cobble clasts.

The Westbury Formation stacked graded rhythmites are interpreted as having formed as a consequence of multiple storm reworking of the sediment producing a succession of graded rhythmites (see also Reif 1982 for Muschelkalk examples). It is worth noting that there is no evidence of unidirectional current activity, implying that the graded rhythmites were indeed formed by wave dominated processes.

Interestingly there is no evidence of bioturbation, even in the upper storm packet; which suggests that a macrofauna was not able to colonize the sediment (presumably either because of high hydrogen sulphide pore water concentrations and/or a lack of oxygen, see below). Consequently it is likely that the shells were transported into the site of deposition (at least over a short distance) rather than just being washed out of their burrows. It is recognized that in this context storms that rework the underlying sediment would also destroy any burrows that were present, however as individual storm events tended not to rework the whole unit (as indicated by the partially superimposed stacked couplets), burrows if present would at least be expected to have their bases preserved.

The effects of storm scour have been modified by algae in Bed 2 at Aust, as the algal laminae appear to have partially stabilized the sediment and prevented its entrainment.

The micritization of the shell fragments was almost certainly caused by algal rather than fungal infestation. This suggestion is likely as modern fungi are not H_2S tolerant (G. Hendry pers. comm. 1986) which would have been a pre-requisite as the sediment was almost certainly anoxic (no bioturbation) and sulphidic (presence of early pyrite, particularly in microenvironments). Consequently the presence of algae suggests that the sediment was deposited in the photic zone, presumably in depths less than 30m. (Bathurst 1975, Golubic *et al.* 1975 and Kobluk and Risk 1977). Further as storm winnowing was only an intermittent process it is likely that water depths were in excess of the fair weather wave base, thus it is concluded that water depths were between 15 and 30m. during the deposition of the calcarenaceous sandstones.

Diagenesis.

The absence of shell and detrital K feldspar etching in the calcarenaceous sandstones, in contrast to the calcareous sandstones (see section 3.2), suggests that the early pore waters never became acidic. Aciditiy in the context of the calcareous sandstones was probably a byproduct of aerobic respiratory processes. As bioturbation is absent from the calcarenaceous sandstones it is assumed that O_2 concentrations were low enough to prevent/severely limit macrofaunal colonization, hence there was no significant carbonic acid production.

The earliest preserved phase of diagenesis in the calcarenaceous sandstones is the precipitation of non-luminescing K feldspar overgrowths around the bright luminescing K feldspar cores. K feldspar precipitation requires alkaline pore waters with high concentrations of silicon, aluminium and particularly potassium ions (Kastner 1971). In this case these ions were probably either supplied from the dissolution of metastable detrital clays e.g. kaolinite and illite or from sea water.

The early evolution of alkaline pore waters in the Westbury Formation may have the consequence of a number of processes e.g.:-

i) Early ammonification of amino acids as a result of bacterial oxidation processes in the surrounding organic rich muds (Berner 1982).
ii) Detrital iron reduction (Curtis 1980).

Following the precipitation of the K feldspar overgrowths, the bulk of the porosity was then infilled by calcareous mud, non-ferroan calcareous spar and locally by pyrite. Following this infill the different calcareous components inverted to non-ferroan bright luminescing calcite and recrystallized. Consequently the bivalves either exhibit pseudopleochroic textures or are only preserved as ghosted outlines defined by their micrite envelopes. The pore filling calcite recrystallized to non-ferroan, bright luminescing microspar or pseudospar, with micrite patches, and the dolomite clasts de-dolomitized. It is likely that this recrystallization occured in the sulphate reduction zone (rather than in a freswater environment as in Folk 1974) where metastable carbonate species invert to non-ferroan calcite in the presence of H_2S, (Walter 1986) and any Fe(II) that is present is mopped up to produce pyrite. This is indicated by the presence of abundant pyrite both as a cement and a replacement mineral for some of the bivalves (after Irwin 1979). It is worth noting that the diassociation of hydrogen sulphide into its component ions causes a pH drop, however it is likely that the pore waters were extensively buffer in the immediate vicinity of this process by shell dissolution, hence there was not a general pH drop in the pore waters, in any case excess H_2S may have been liberated as a gas.

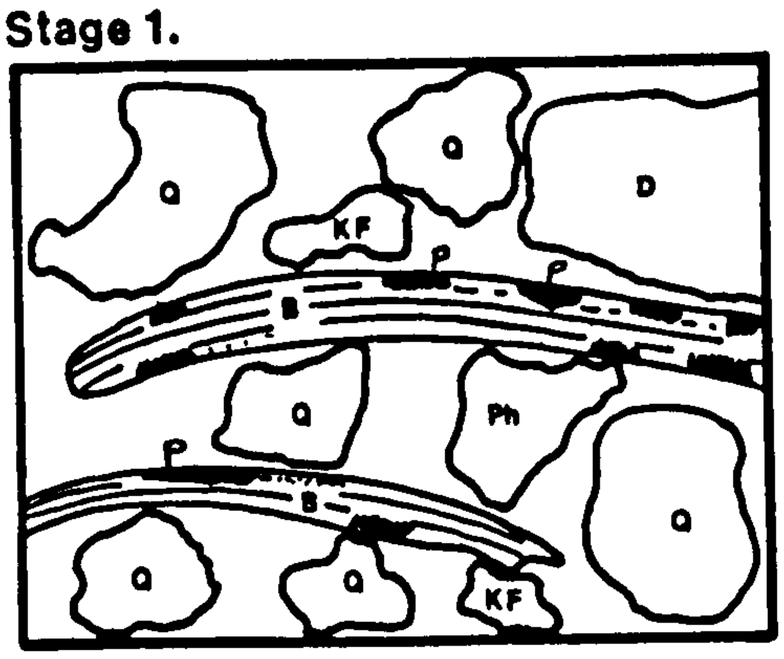
As a final comment it is interesting to note that the phosphates in the calcarenaceous sandstone facies appear not to be zoned, this either implies that pore water phosphate concentrations were low (as a result of phosphate flux out of the sediment) or conditions were not suitable for phosphate precipitation (possibly because the pH's were in excess of 7.8 where calcium carbonate will precipitate) or both. Thus any phosphate enrichment that did occur probably did not happen in-situ and thus the phosphatic bone debris and coprolites must have

been reworked into this lithofacies. Therefore, unlike the calcareous sandstones, the pore waters associated with the calcarenaceous sandstones never became significantly acidic during burial.

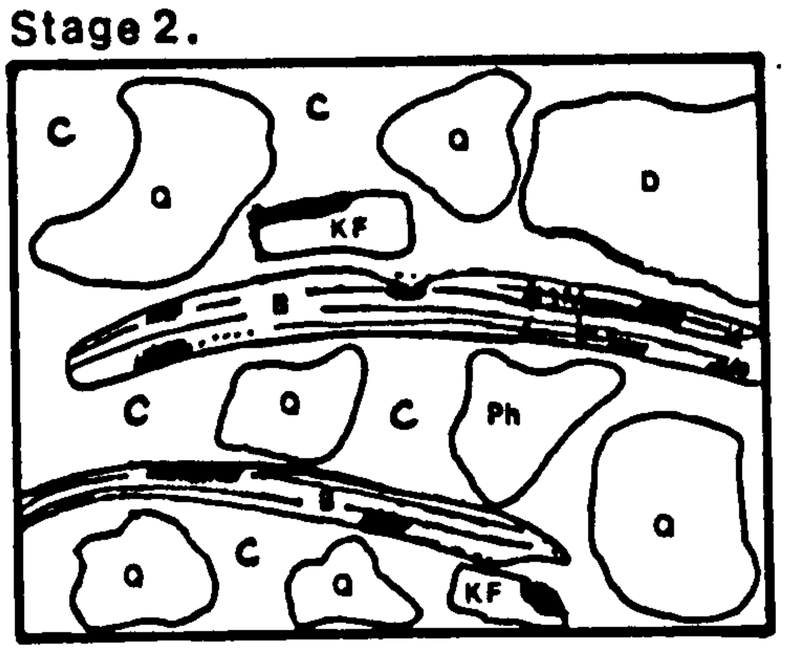
The diagenetic history is summarized in figure 3.6.

Figure 3.6.
Stage 1, Marine phreatic, with low/no oxygen concentrations. Depositon of sand grade quartz, K feldspar, calcitic and phosphatic debris with some re-worked dolomite clasts. Algal boring causes localized sulphidic conditions which produces pyritized micrite envelopes.
Stage 2, Early diagenesis, anaerobic zone. Indeterminate carbonate infilling of primary porosity, and K feldspar overgrowth formation. Alkaline pore water conditions.
Stage 3, Deeper diagenesis, sulphate reduction/post sulphate redction zone. Recrystallization of metastable carbonate producing:- pseudograinstone fabrics, pseudopleochroic textures in the bivalves, and de-dolomitizing the dolomite grains. Local replacement of some of the bivalves and pore filling calcite by pyrite

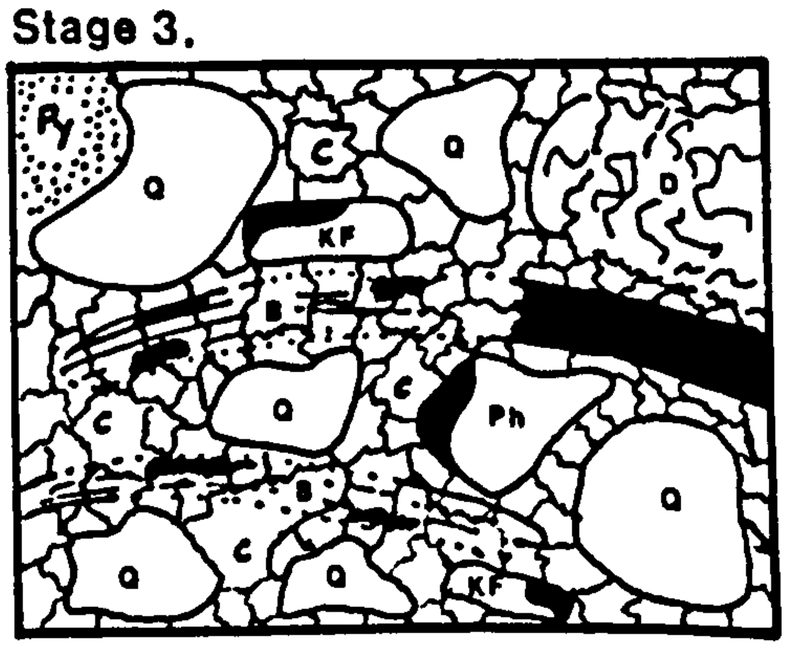
Stage 1.



Stage 2.



Stage 3.



Section 3.4a. Packstones.

Packstones are common in the Westbury Formation and often alternate on a sub-millimetre scale with other facies forming facies couplets e.g. calcareous sandstones (plate 3.32). The packstones are composed of reworked, predominantly convex-up (plate 3.38), occasionally end-on (plate 3.39) crushed bivalves (e.g. plate 3.40) and sand grade quartz (plate 3.41), in a calcareous microspar matrix (plate 3.38, plate 3.39)). In addition they contain minor amounts of :- clay grade kaolinite and illite (figure 3.7), glauconite, sand grade K feldspar with overgrowths (plate 3.42), reworked gastropods (plate 3.41), brachiopods (plate 3.43), ostracods (plate 3.44), spherulites (plate 3.45), echinoderm plates (plate 3.46) and phosphatic debris (plate 3.40).

The interstital calcareous mud drapes the shell debris and partially infiltrates the underlying sediment (plate 3.38), thereby preserving shelter porosity with mud geopetals (plate 3.39). This shelter porosity has been infilled by zoned calcite spars (plate 3.47) which are composed of bright luminescing, non-ferroan (zone I and zone II) calcite which may contain dispersed pyrite (plate 3.48) and ferroan, dull luminescing (zone III) calcite (plate 3.49). An individual pore is not necessarily filled with all of these three calcite zones (e.g. plate 3.50 where only zones I and II are present and plate 3.51 where outside the gastropod whorl I and III are present and inside just II).

The bivalves are usually composed of non-ferroan (e.g. plate 3.38 and plate 3.39), medium luminescing calcite (plate 3.49) and exhibit pseudopleochroic textures (plate 3.40). Locally, however, they have been replaced by ferroan structureless dull luminescing calcite (plate 3.50). The shells themselves are frequently micritized, with the micrite envelope being pyritized (plate 3.40), and at some localities they contain larger (<50 um.) flask shaped borings (plate 3.42) (often also pyritized). Locally the shelly material is surrounded by non-ferroan (plate 3.52), bright luminescing, calcareous grain coats (e.g. plate 3.53).

Some of the primary pore filling calcite has recrystallized to pseudosparry calcite (e.g. plate 3.54) and contains remnant micrite patches (plate 3.55).

At some localities the packstone horizons are overgrown by displacive vein calcites (plate 3.56), which display cone-in-cone fabrics (plate 3.57). Within these units dissolution is often intense, clays are often concentrated on dissolution seams and recrystallization has obscured many of the primary textures (plate 3.58).

Figure 3.7. X-ray spectra of the untreated, glycolated and heated <2um. fraction from Aust 9. The dominant clay present is illite (peak labeled I). Quartz is also present (Q) in this fraction. Glycolation and heating have had little effect on any of the peaks.

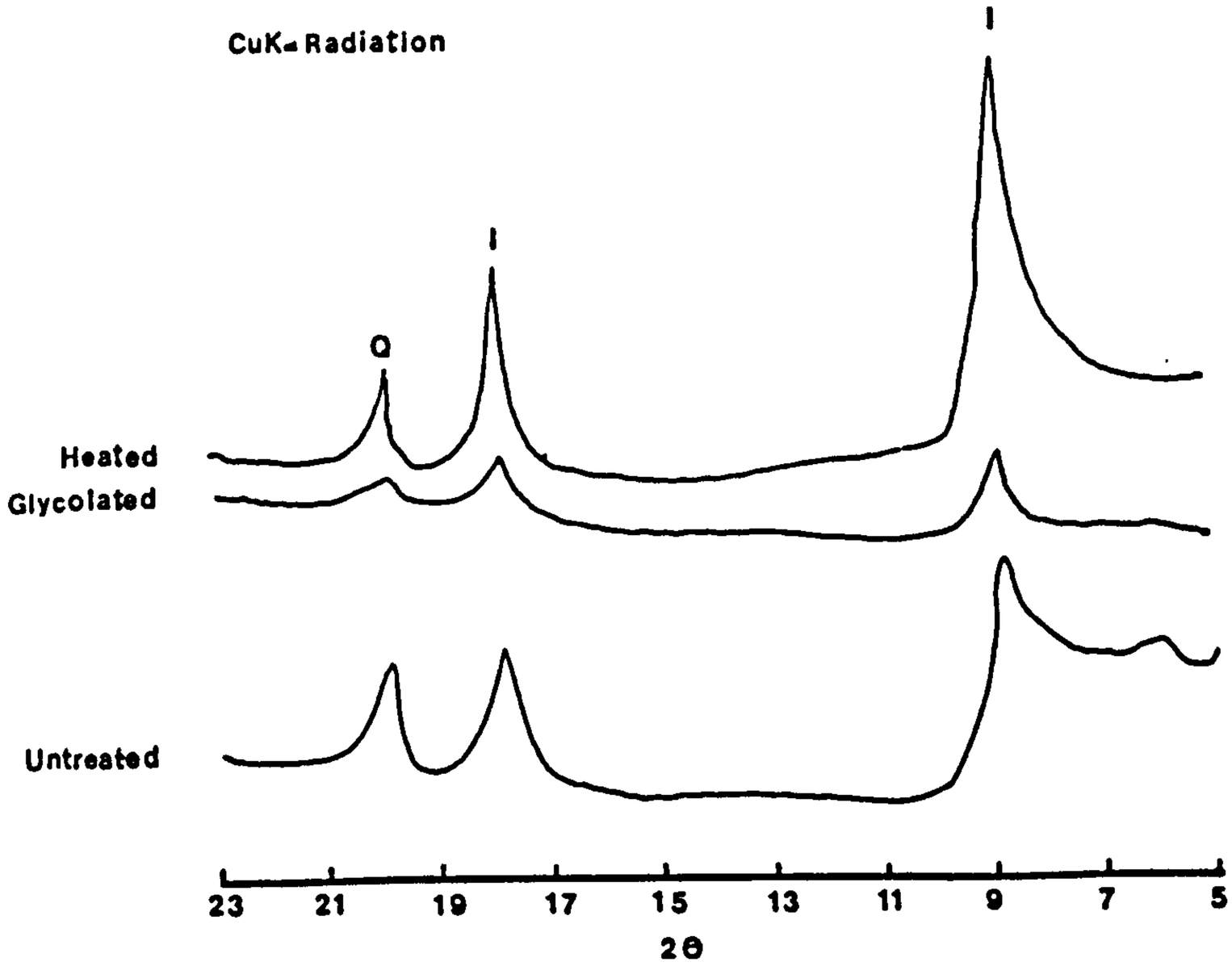


Plate 3.38. Biolithoclastic packstone (p.p.l.).
Disarticulated bivalve debris (Bv) preserved in a non-ferroan calcareous microspar, from St. Audries 7. Shelter porosity has been preserved beneath the bivalves which has been partially filled with carbonate mud (M), forming mud geopetals (Ge). The remaining porosity has been infilled with non-ferroan calcite (NFC).

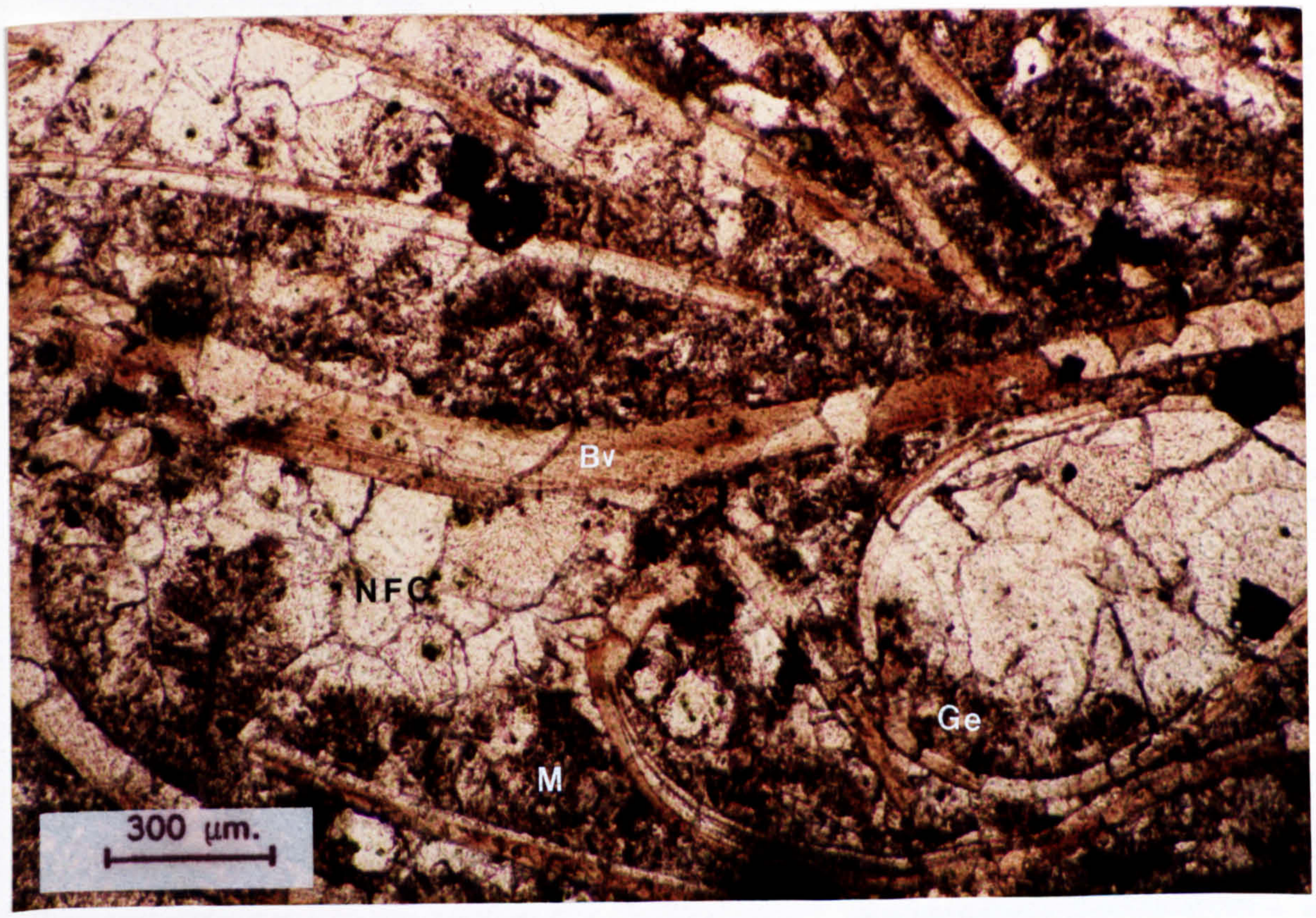


Plate 3.39. Biolithoclastic packstone (p.p.l.).
Biolithoclastic packstone containing recrystallized bivalves (Bv), sand grade quartz (Q) and glauconite pellets (G) in a micrite matrix (M), from St. Audries 7. Where the mud has not completely infiltrated the sediment shelter porosity has been preserved, which has been infilled with a non-ferroan calcite spar (NFC). The bivalves are preserved disarcticulated, convex-up and end-on and exhibit pseudopleochroic textures. Locally pyrite replaces some of the calcite.

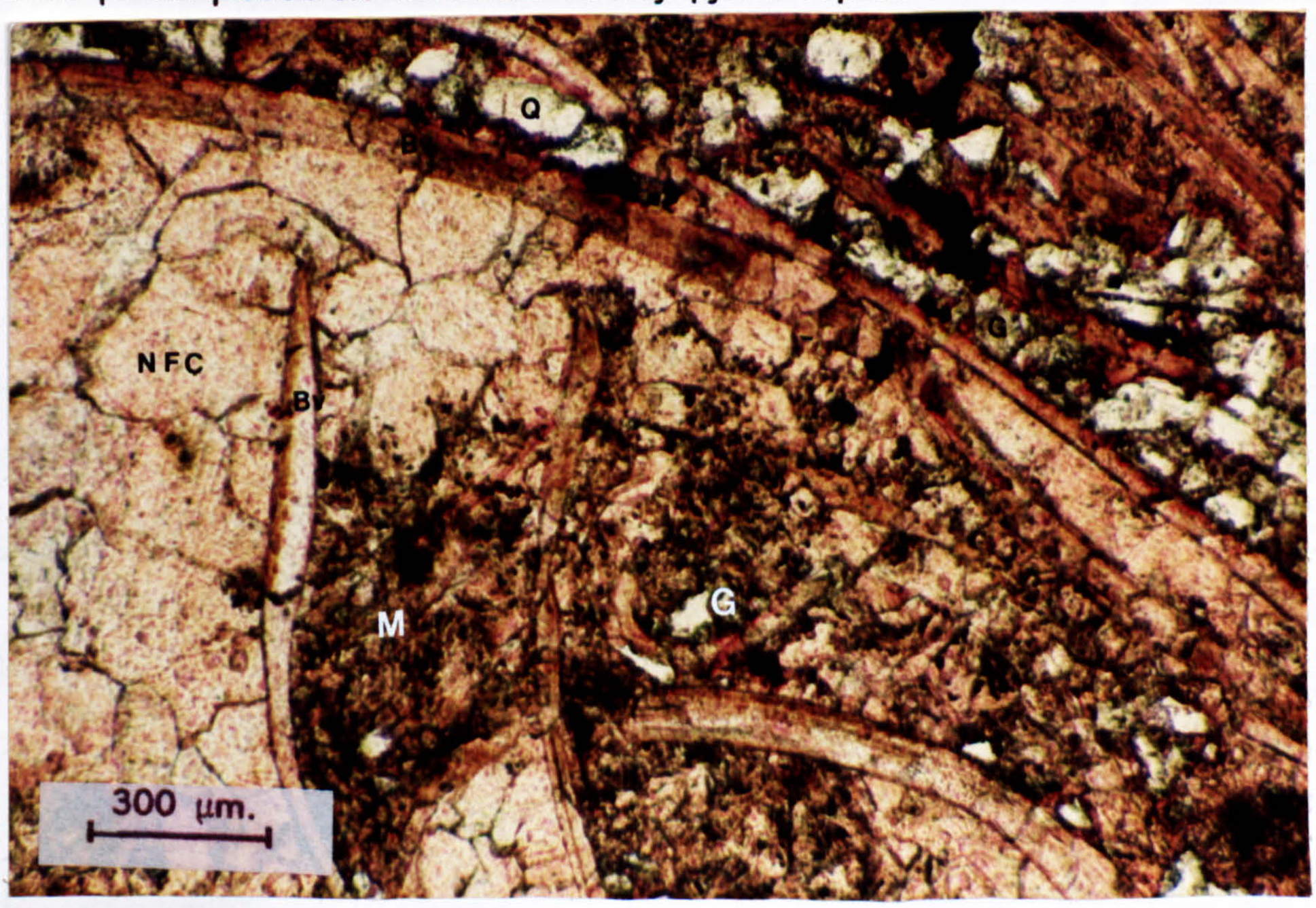


Plate 3.40. Bioclastic "pseudograinstone" (p.p.l.).
Broken, recrystallized bivalves (RBv) in a non-ferroan calcareous (NFC) "pseudospar" (PsG), from Watchet Harbour 11. The bivalves exhibit pseudopleochroic textures and have pyritized micrite envelopes, which define the outline of the otherwise invisible recrystallized biogenic fragments. Locally remnant micrite patches (M) are present in the spar. A minor phosphatic component is present (Ph).

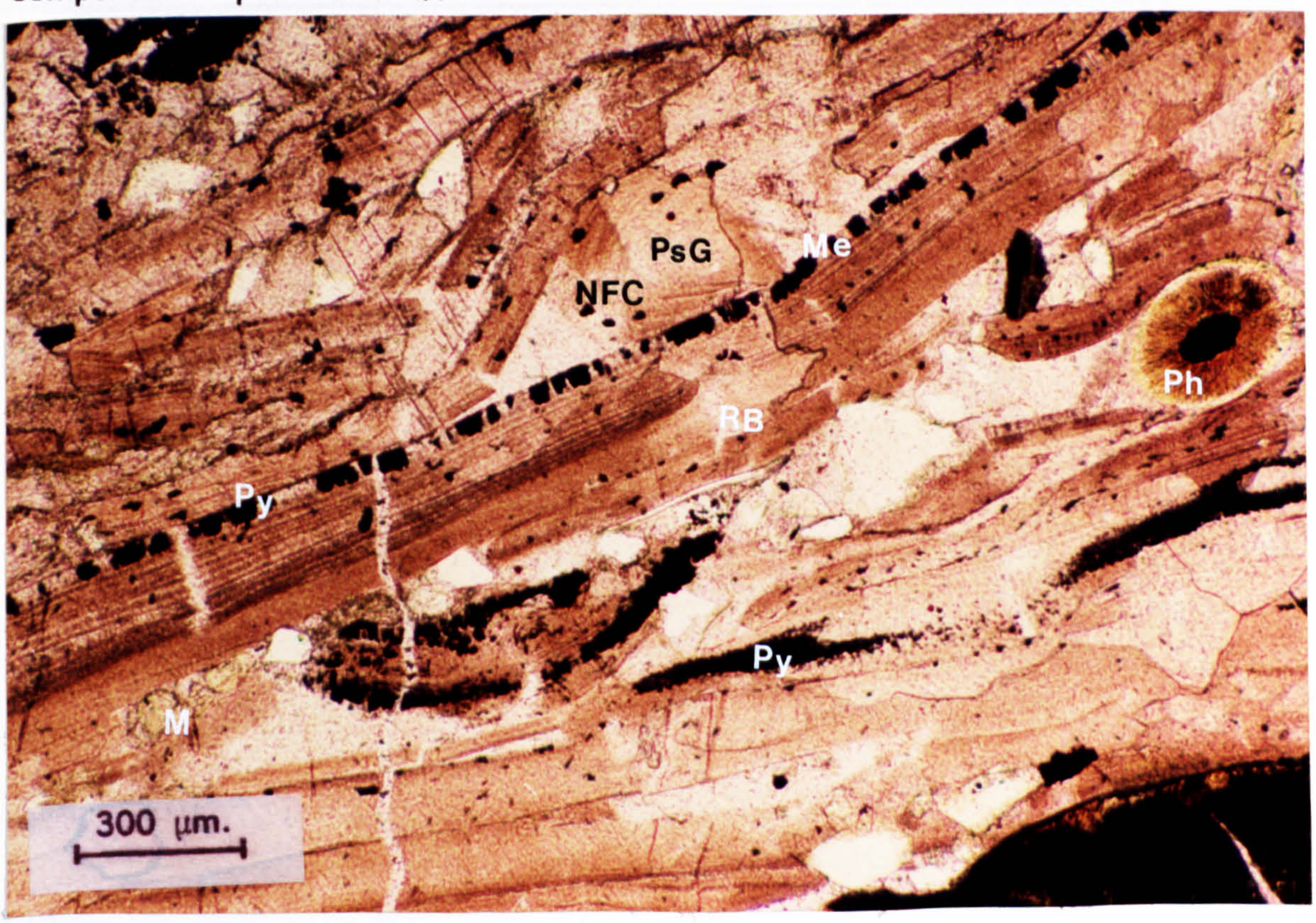


Plate 3.41. Biolithoclastic packstone (p.p.l.).
Bivalves (Bv), gastropods (G) and fine sand grade quartz (Q) in a micrite and glauconite matrix, from Watchet Harbour 3. The bivalves are coated in an inclusion rich non-ferroan calcareous envelope, which is itself coated with a non-ferroan acicular calcite (arrowed A). The bivalve fragments are recrystallized and composed of non-ferroan calcite. (For detail see plate 3.52).

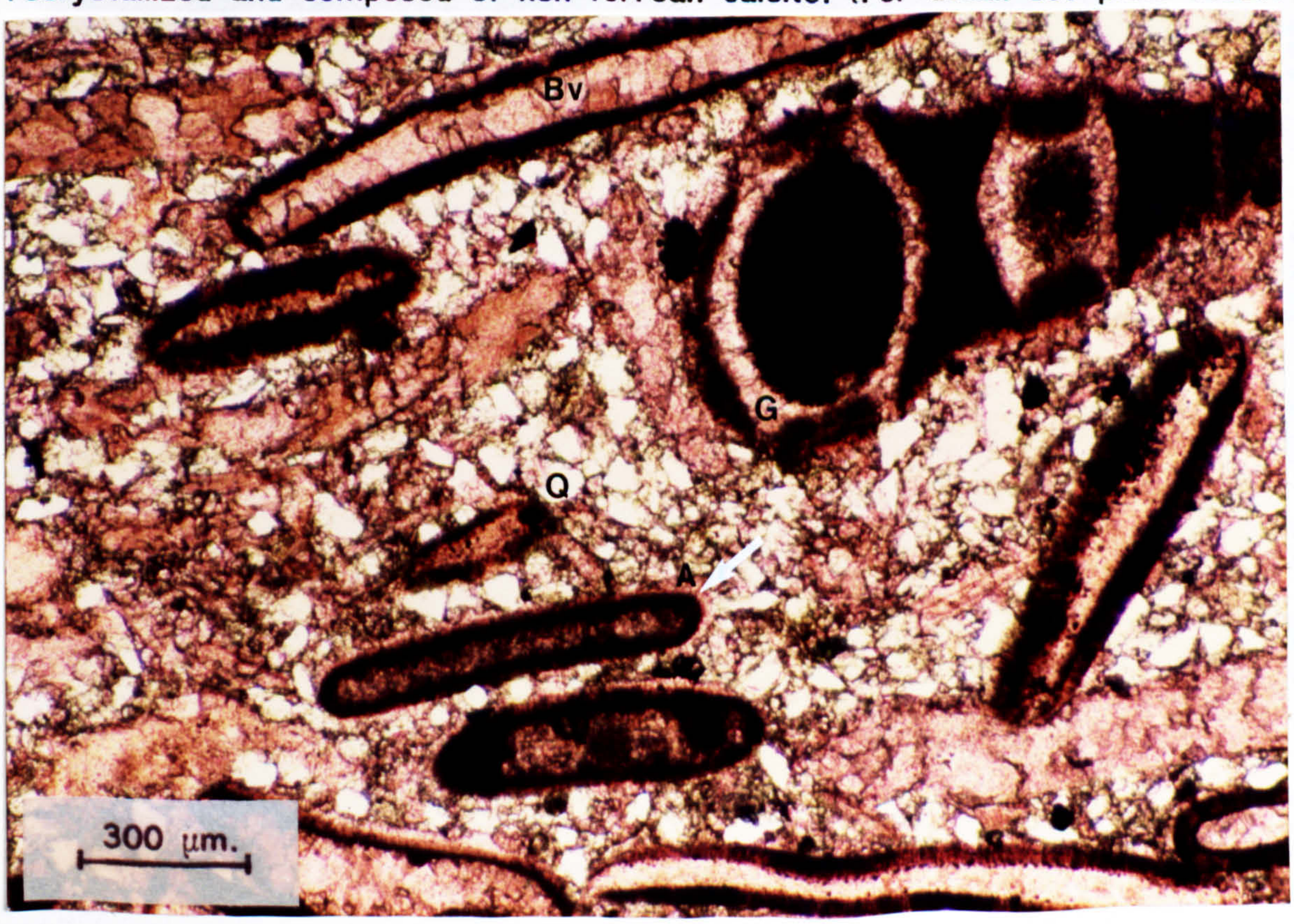


Plate 3.42. Borings in bivalve fragment within lithoclastic packstone (CL.). Biolithoclastic packstone containing abundant bivalve debris (Bv), fine sand grade quartz (Q) and K feldspars (K), in a non-ferroan, bright luminescing calcite matrix, from Watchet Harbour 3. The bivalve fragments (Bv) have been bored (S) and often have well developed grain coats (C). The matrix is unzoned calcareous pseudospar.

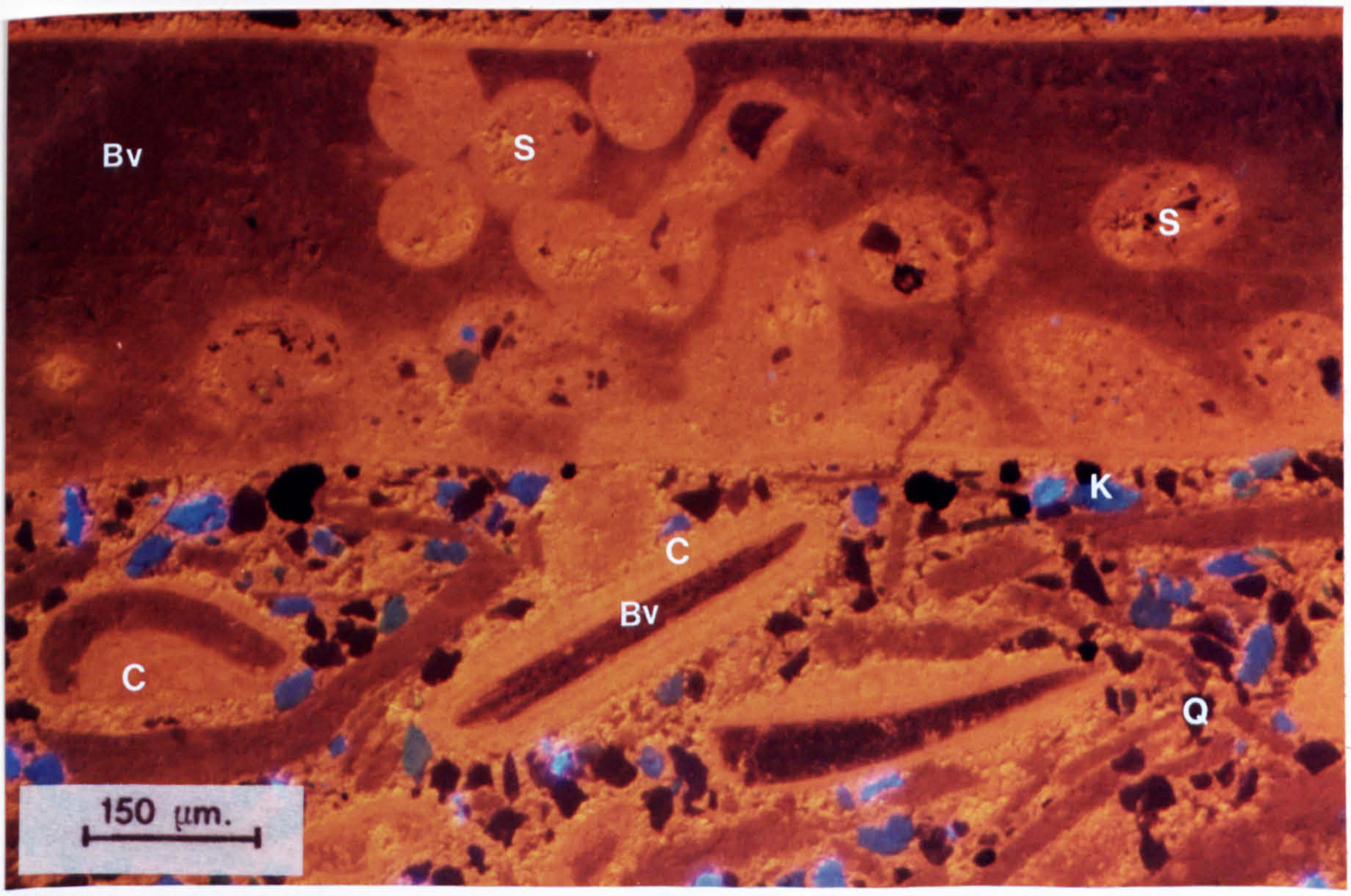


Plate 3.43. Bioclastic packstone (p.p.l.)
Bivalve and brachiopod fragments in a non-ferroan calcareous microspar (Ms), from St. Mary's Well Bay 2. The internal structure of the brachiopod is well preserved with respect to the bivalves (Bv) which are intensely recrystallized, although the brachiopod fragment contains small pyrite filled borings (arrowed).

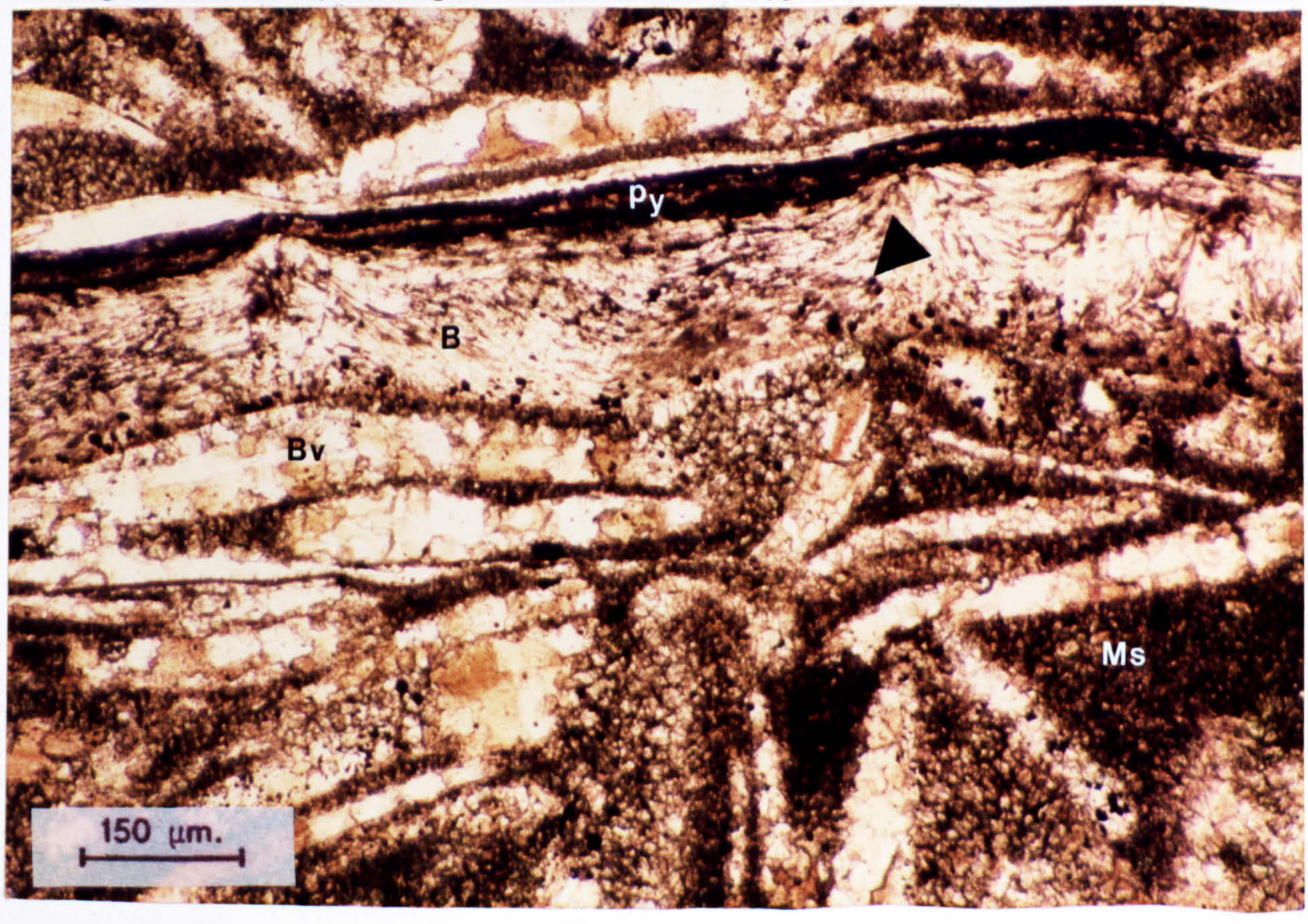


Plate 3.44. Ostracods in bioclastic "pseudograinstone" (p.p.l.).
Ostracod and bivalve debris in a "pseudograinstone", from Aust 9T. The ostracods (O) contain micrite (M) and are composed of non-ferroan calcite. The bivalves have been recrystallized (RB) and are barely visible in the pore filling spar - some have pyritized micrite envelopes (Py). Some of the grains are surrounded by a acicular calcite (arrowed).

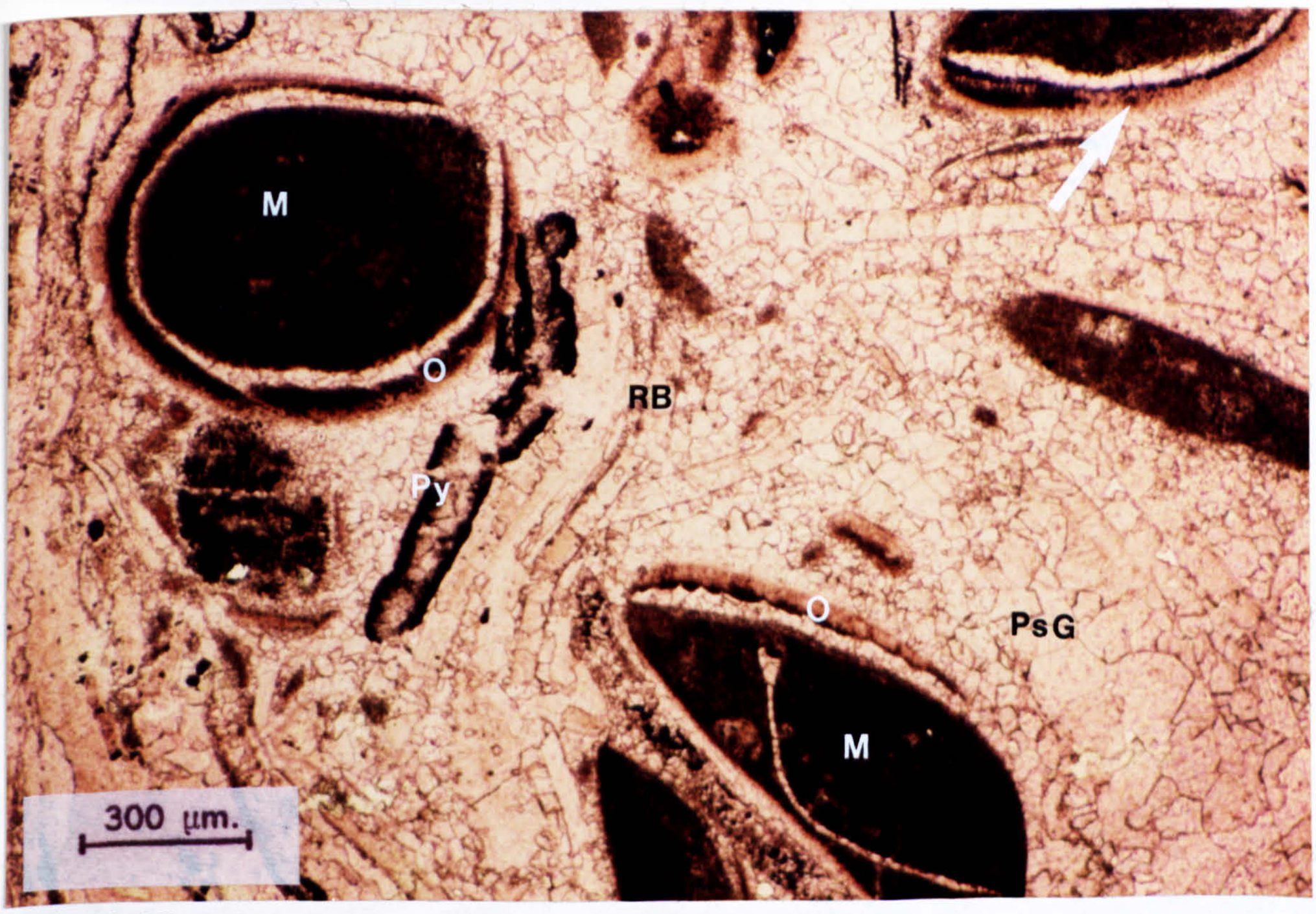


Plate 3.45. Spherulites in bioclastic packstone (p.p.l.).
Non-ferroan bivalve debris (Bv) and spherulites (Sp) in a recrystallized pseudospar (Ps), from Wainlode 10. The spherulites appear to be preserved in a remnant micrite matrix (M), apparently within shelter porosity beneath the bivalve debris.

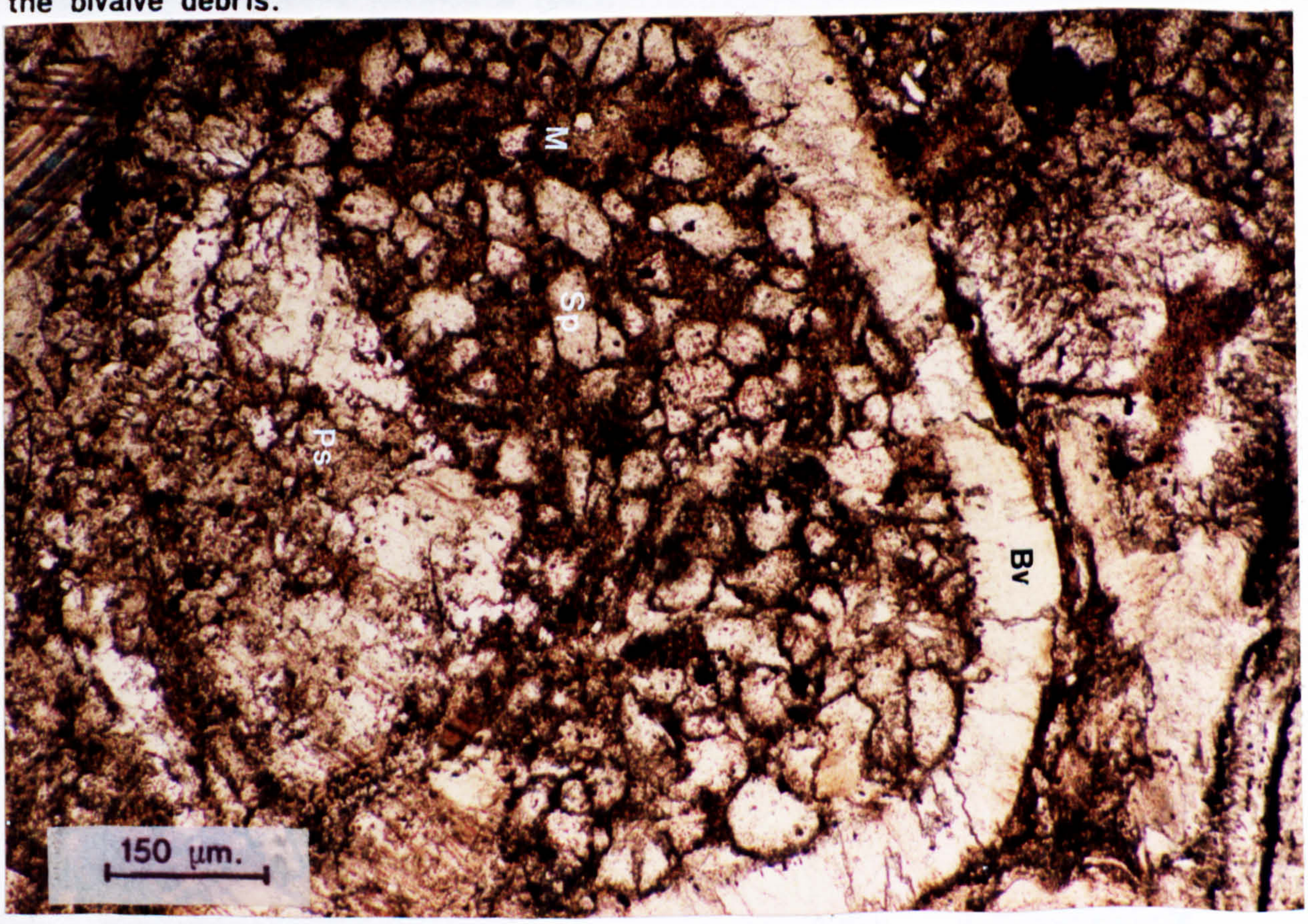


Plate 3.46. Biolithoclastic packstone (p.p.l.).
Biolithoclastic packstone containing detrital quartz (Q), glauconite (Gl), recrystallized bivalve debris (Bv) and disarticulated echinoderm plates (E) in a non-ferroan calcareous microspar, from Watchet Harbour 3. The bivalve debris has recrystallized (some exhibits pseudopleochroic textures) and/or micritized and has been encased in inclusion rich grain coats. The echinoderm plates contain small pyritic inclusions and have been covered by tangential non-ferroan calcite coats (C).

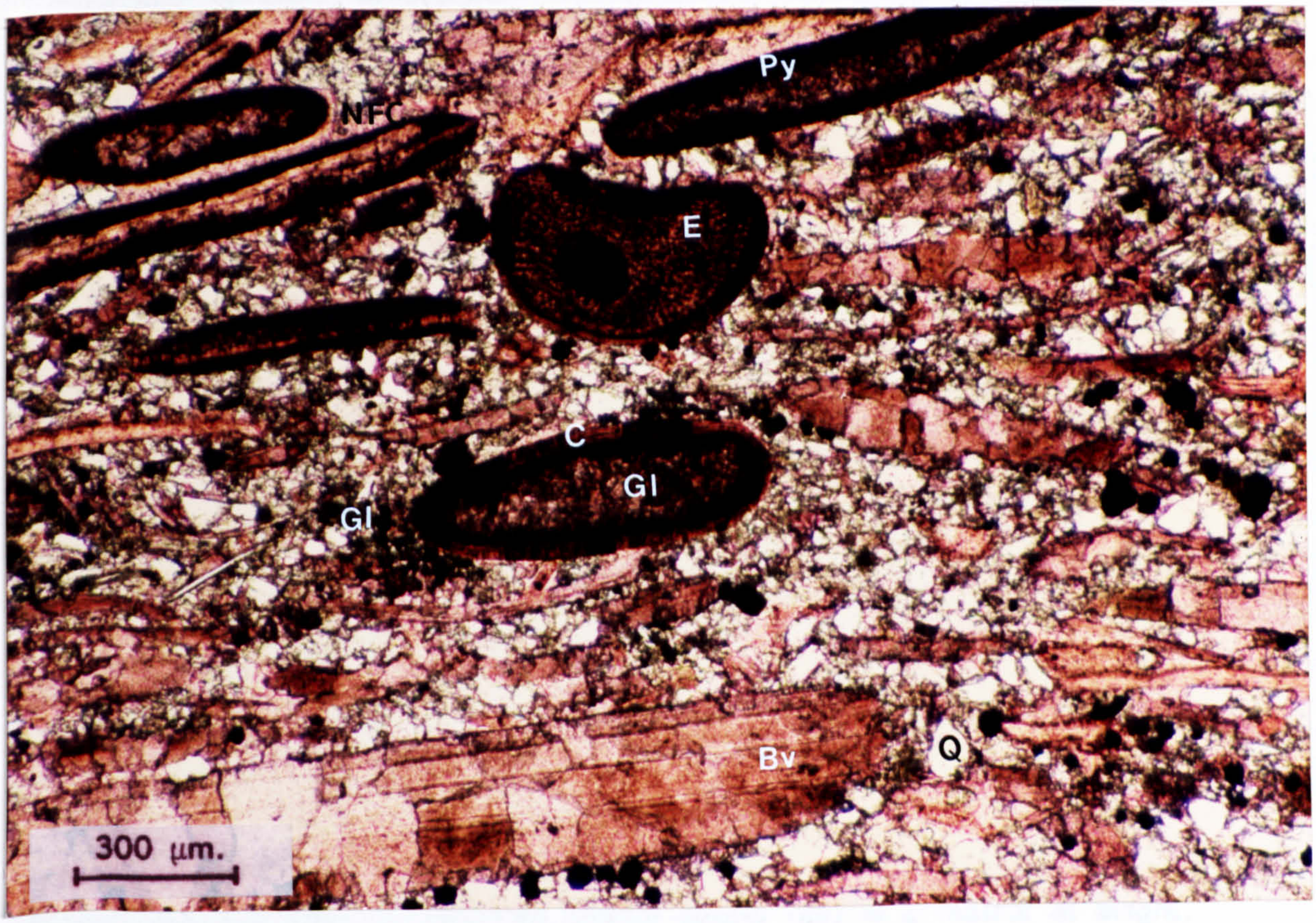


Plate 3.47. Bioclastic packstone (CL.).
Medium/dull luminescing, disarticulated, reworked bivalve debris (Bv) in a bright, blotchy luminescing micrite (M), from St. Audries Bay 7. Shelter porosity is preserved beneath the bivalve fragments. This shelter porosity is initially infilled with bright luminescing zone I calcites (I), which are followed by bright luminescing multizoned calcites (II) and finally by dull luminescing zone III spars (III). A minor detrital quartz fraction is present (Q).

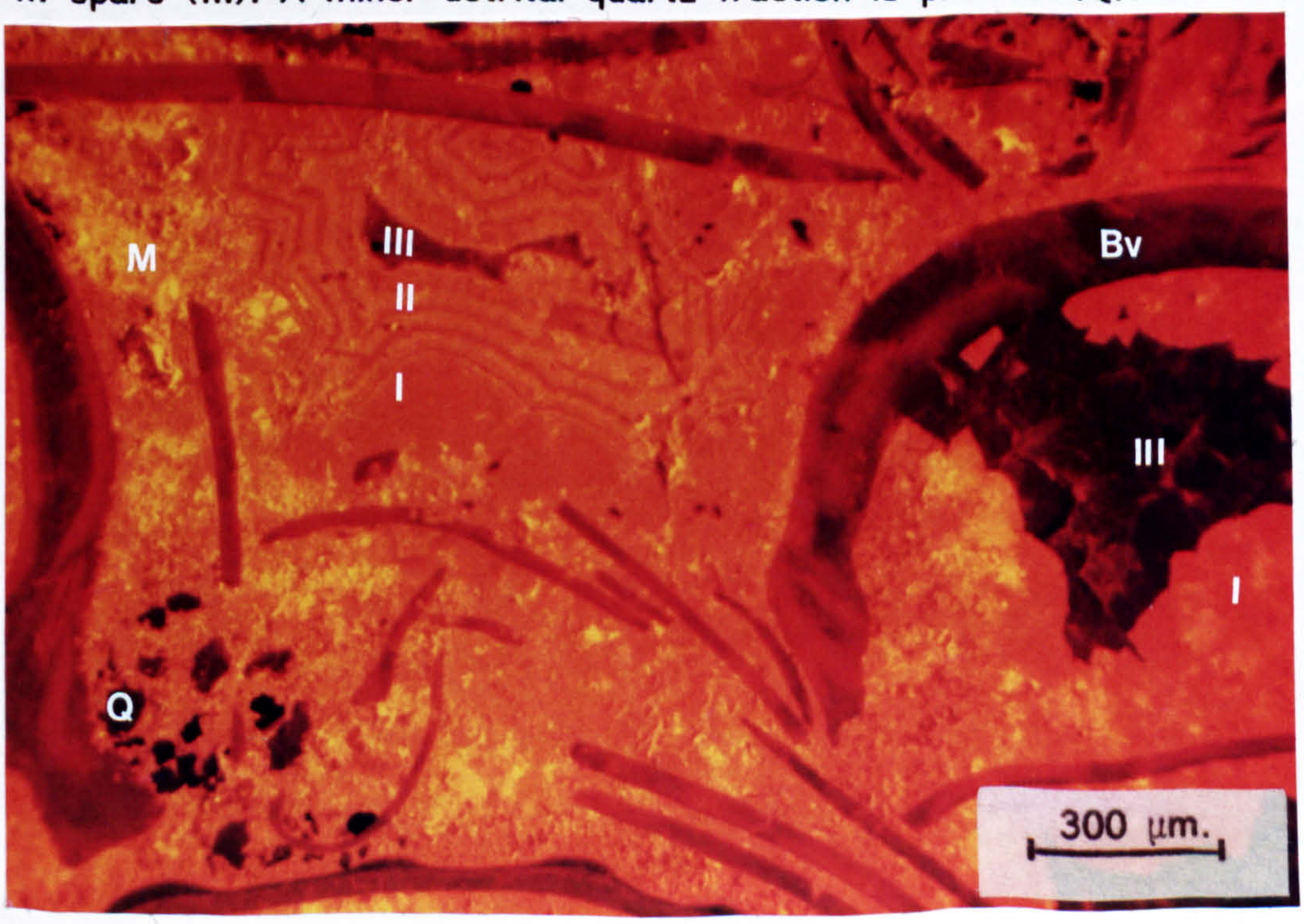


Plate 3.48. Bioclastic packstone (p.p.l.).
Disarticulated, reworked bivalve debris (Bv) in a non-ferroan calcareous microsparry calcite (M), from St. Audries 7. Shelter porosity is preserved beneath the bivalve fragments, which has been partially infilled with mud (forming mud geopetals) (M), but has mainly been infilled with a non-ferroan calcareous spar (NFC) with pyrite inclusions (Py arrowed).

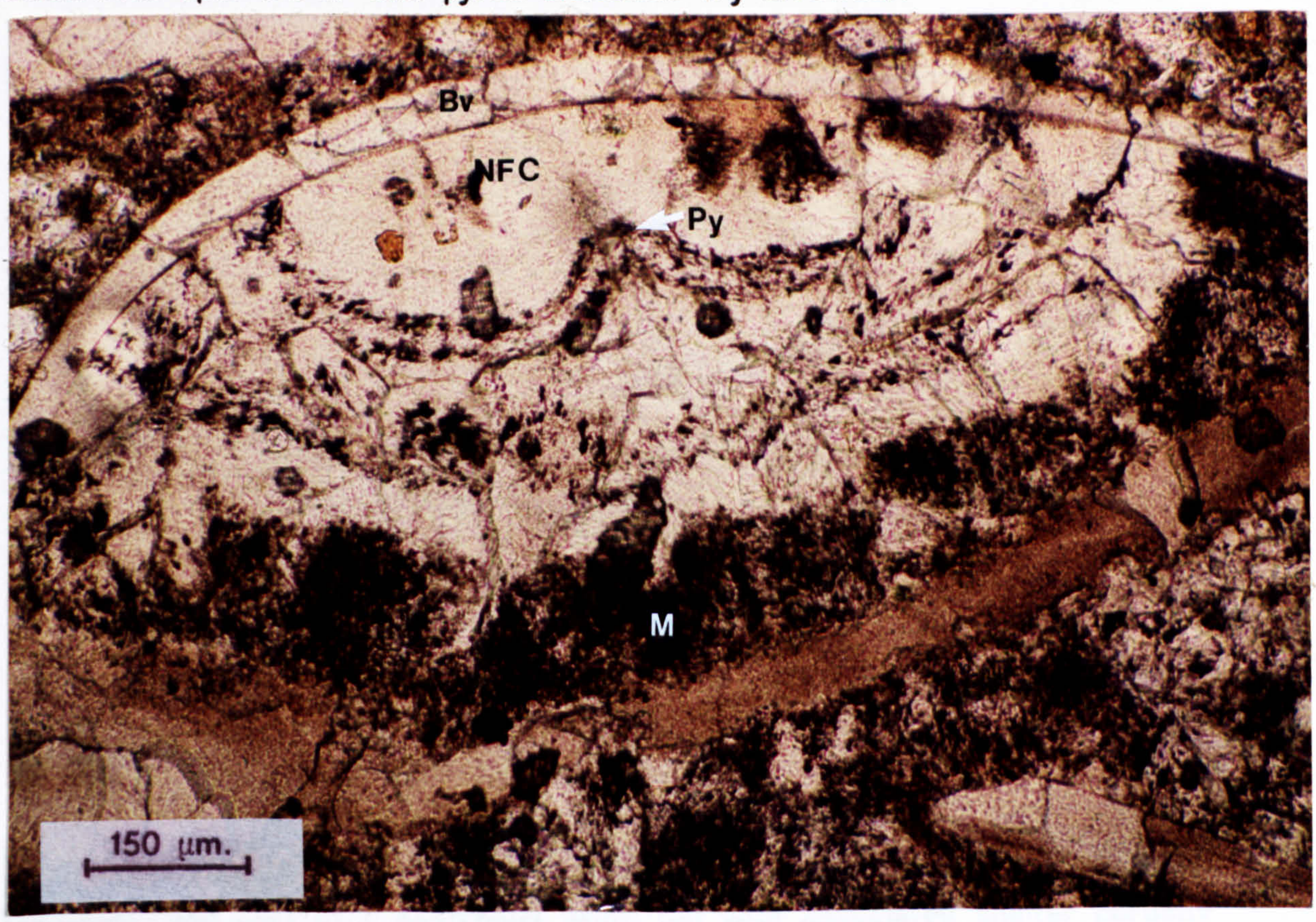


Plate 3.49. Bioclastic packstone (CL.).
Medium/dull luminescing, reworked bivalve debris (Bv) in a matrix of bright, blotchy luminescing microsparry calcite (Ms) with minor amounts of K feldspar (with overgrowths), from St. Audries 9. Shelter porosity is preserved beneath the bivalves and is infilled initially by medium/bright zone I spar (I), and latterly by dull luminescing zone III spar (III).

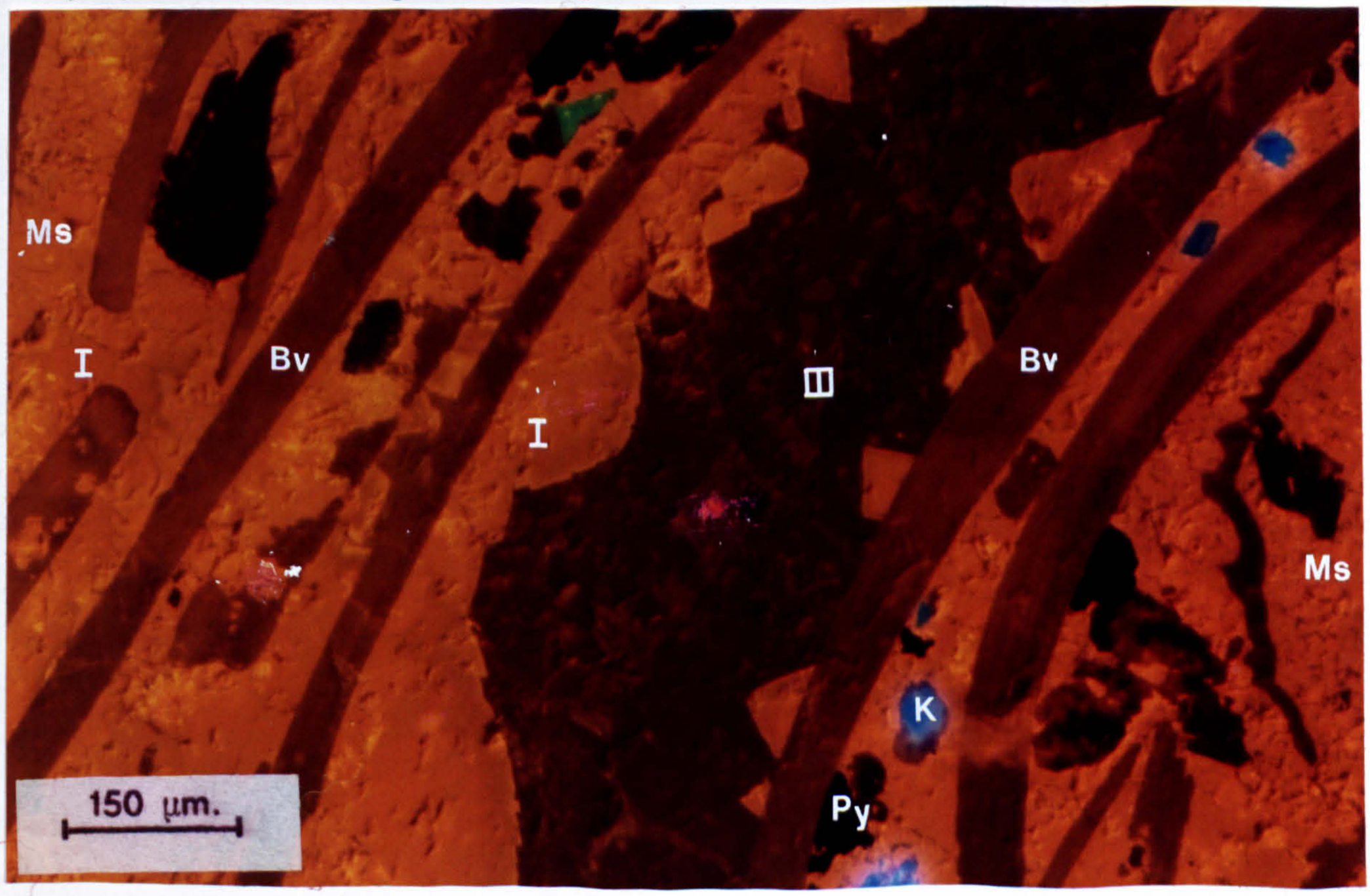


Plate 3.50. Bioclastic packstone (CL.).
Reworked, dull luminescing bivalves (Bv) in a blotchy, bright luminescing microsparry calcite, from St. Audries 7. Shelter porosity is preserved beneath the bivalves. This shelter porosity is initially infilled with medium luminescing zone I calcite spar (I) and latterly by multizoned medium/bright luminescing zone II spar (II).

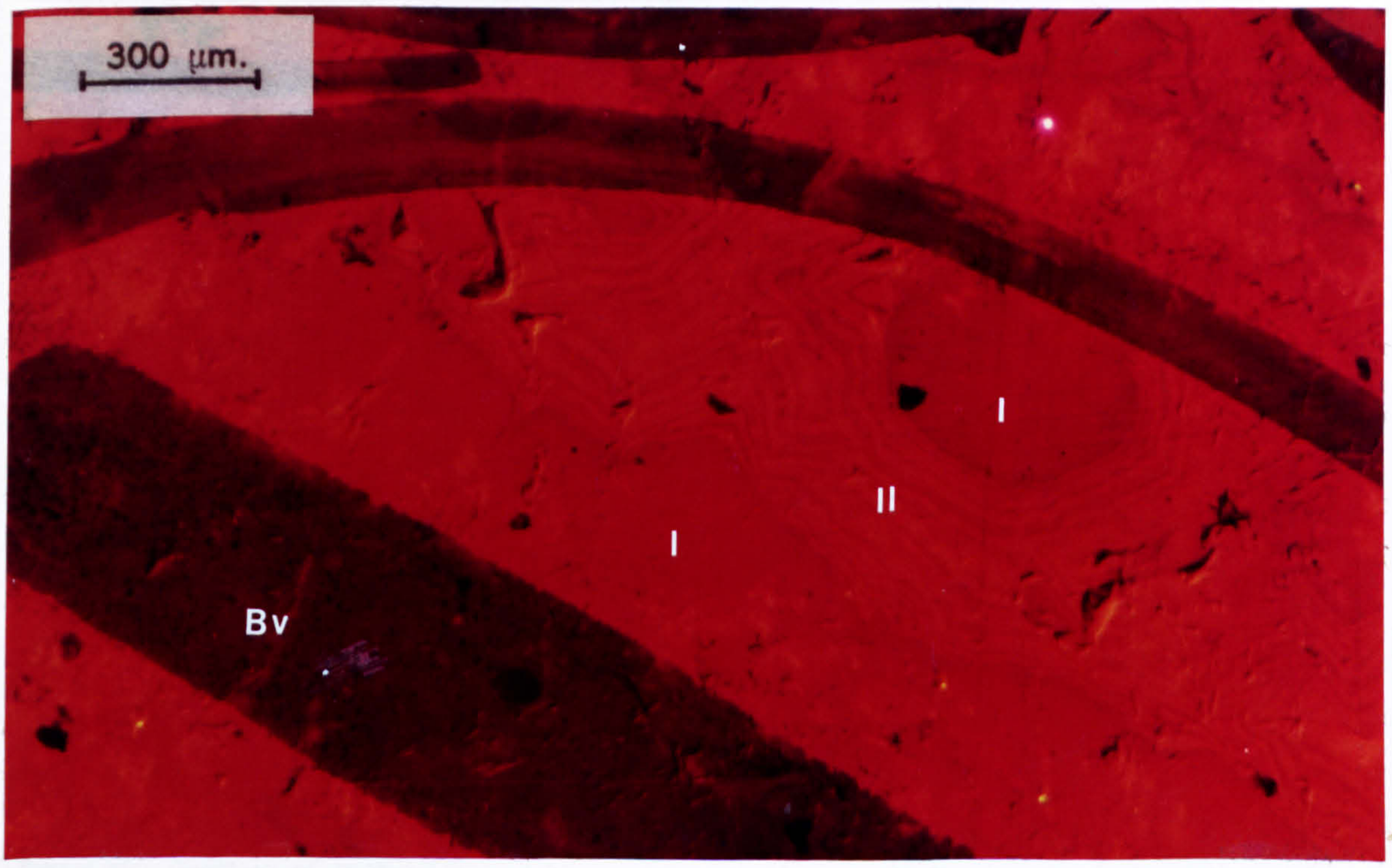


Plate 3.51. Bioclastic packstone (CL.).
Dull luminescing reworked bivalve debris (which exhibits pseudopleochroic textures), and part of a gastropod whorl (G) with associated shelter porosity sparry calcite, from St. Audries 7. The inside of the gastropod whorl is infilled by bright luminescing, multizoned II spar (II), whilst outside there are bright luminescing zone I (I) and dull luminescing zone (III) sparry calcites. Interestingly the bivalve debris has similar luminescence characteristics to the zone III cements (arrowed).

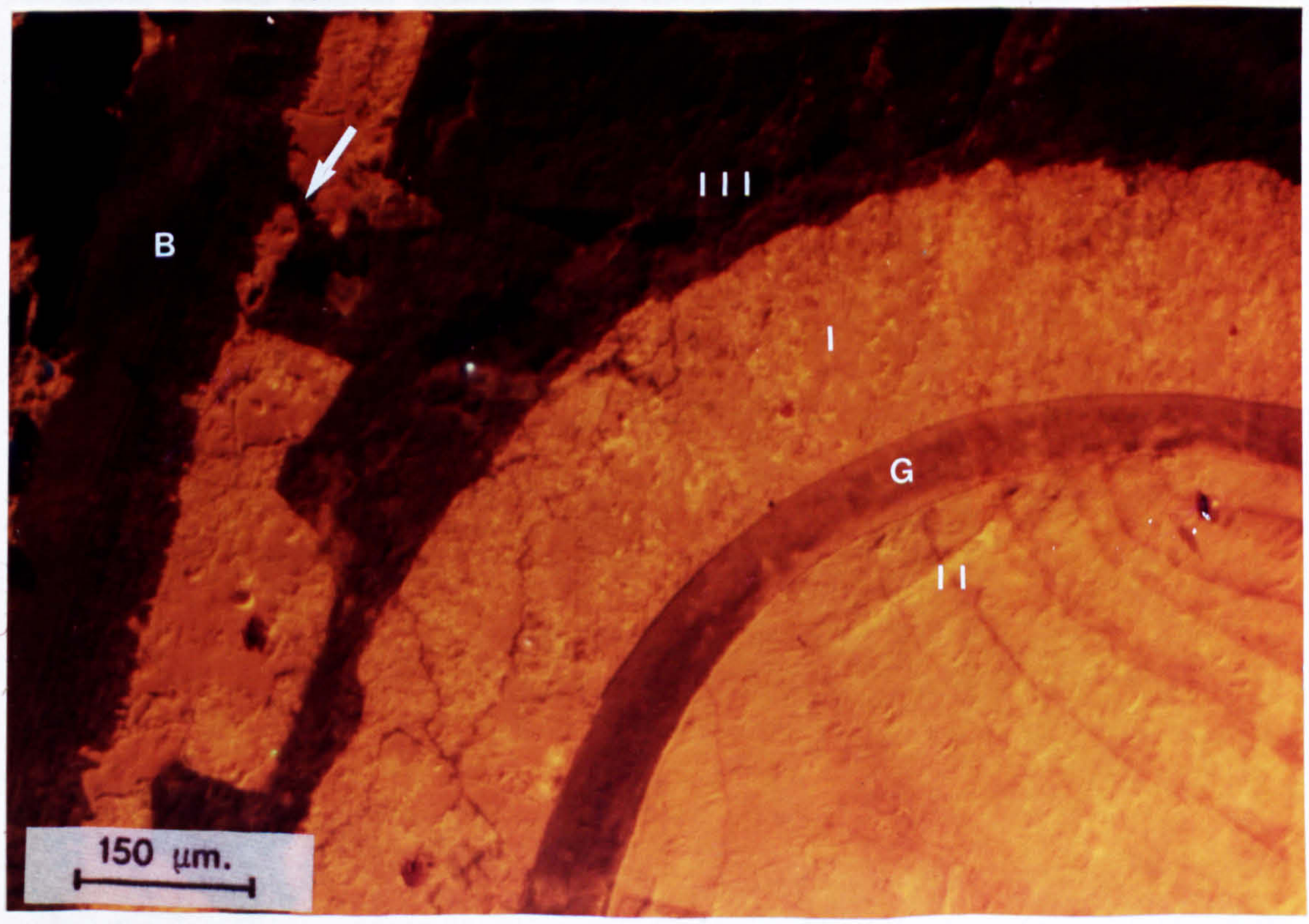


Plate 3.52. Bioclastic packstone (p.p.l.).
Recrystallized, grain coated bivalve debris in a matrix of glauconite (Gl) and non-ferroan inclusion rich microsparry and sparry calcite, from Watchet Harbour 3. The bivalves are composed of non-ferroan calcite and exhibit no internal textures. Some of the fragments are surrounded by an inclusion rich tangential non-ferroan calcite grain coat (C). This grain coat is itself surrounded by an acicular non-ferroan calcite spar (A).

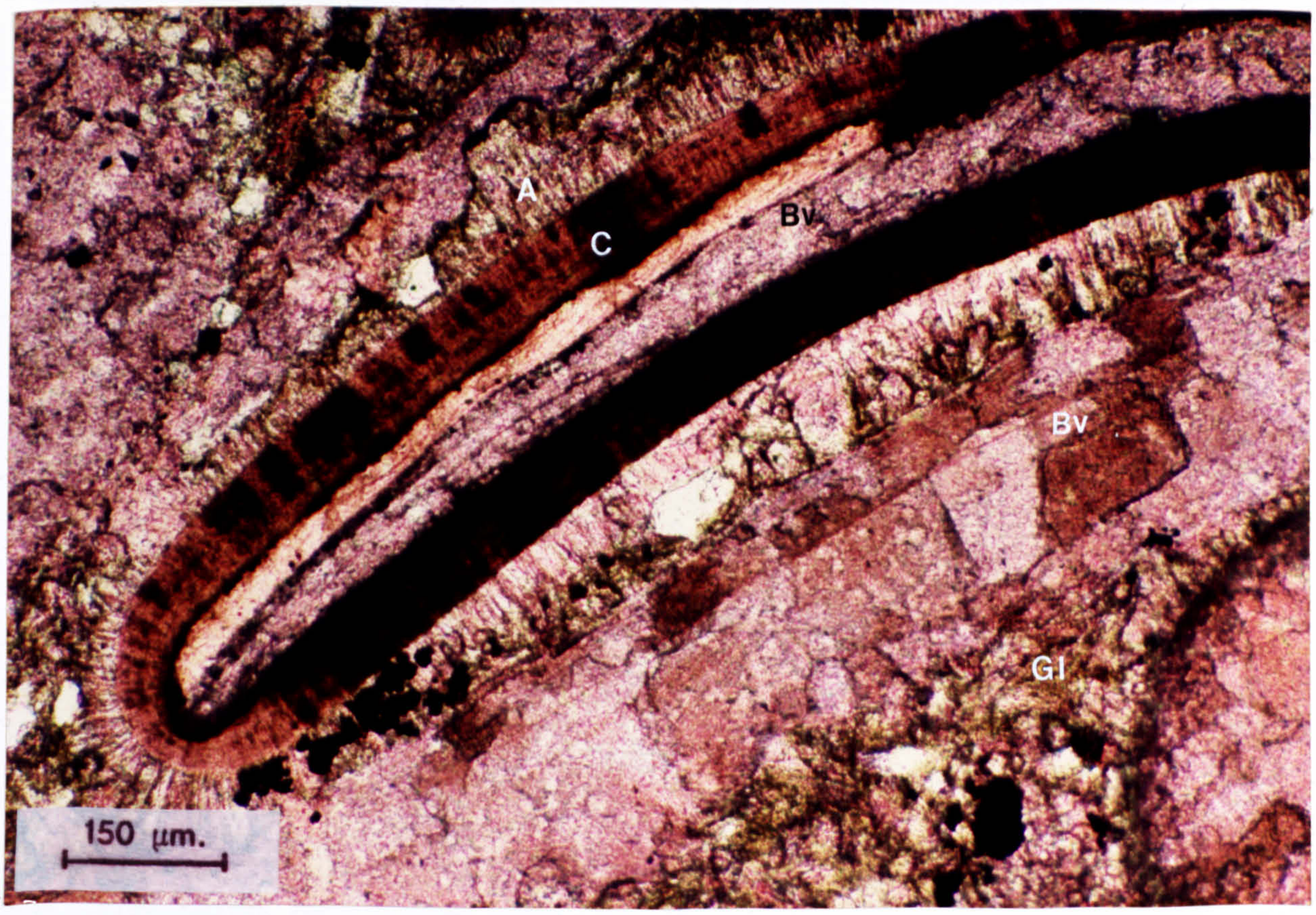


Plate 3.53. Bioclastic packstone (CL.).
Medium/dull luminescing bivalve (Bv) and echinoderm (E) debris in a matrix of medium/bright luminescing calcareous microspar (Ms), from Watchet Harbour 3. Some of the bivalve debris is sheathed in a medium luminescing grain coat (C). This grain coat is surrounded by a bright luminescing acicular calcite (I). The rest of the primary porosity is infilled with a medium luminescing calcareous spar (III). Minor amounts of K feldspar (K) and quartz (Q) are present.

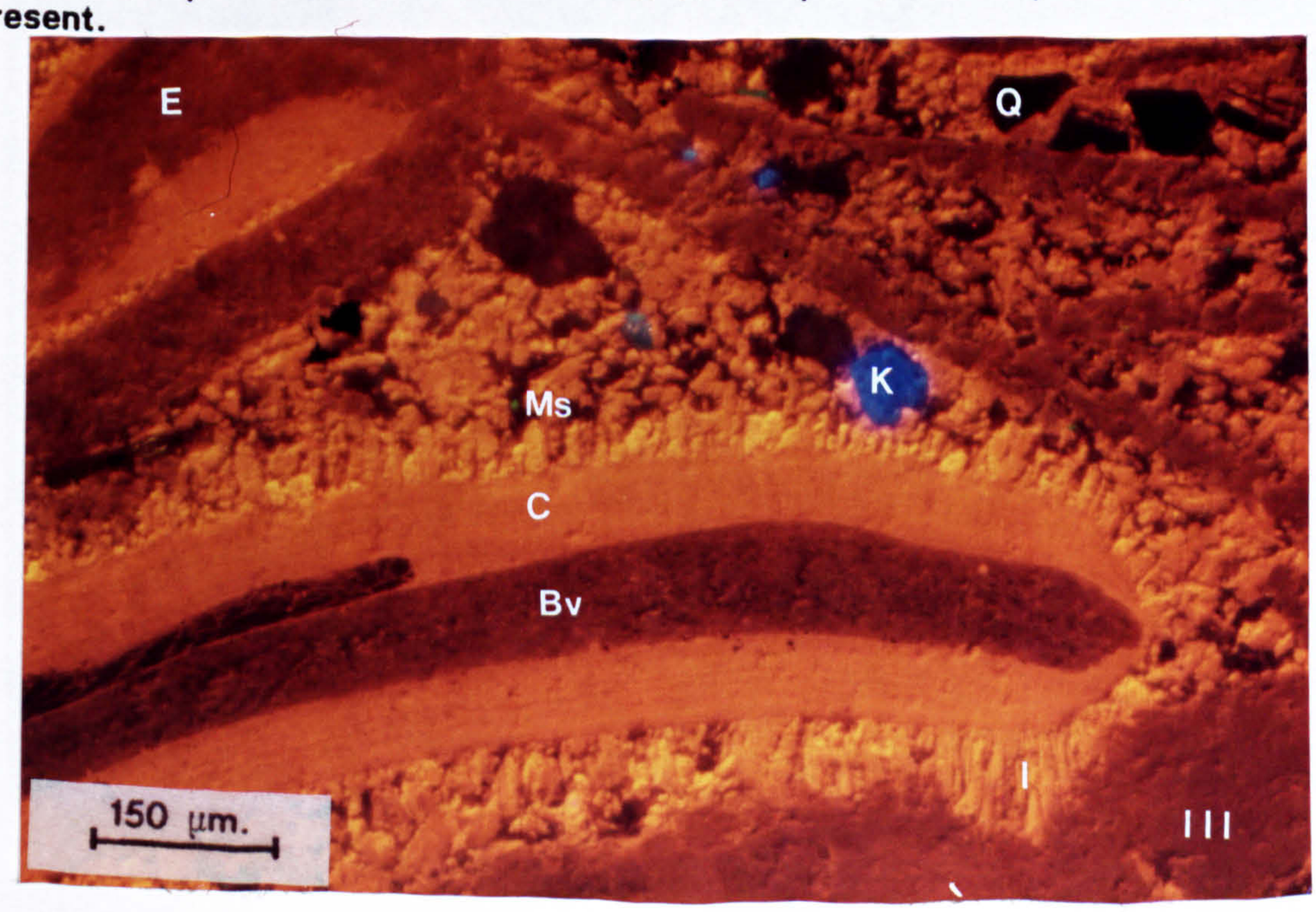


Plate 3.54. Bioclastic "pseudograinstone" (p.p.l.).
Recrystallized bivalve (Bv) and echinoderm (E) debris in a non-ferroan, recrystallized calcareous matrix (PPs), from Aust 9. Some of the bivalve debris has been micritized and their micrite envelopes have been pyritized.

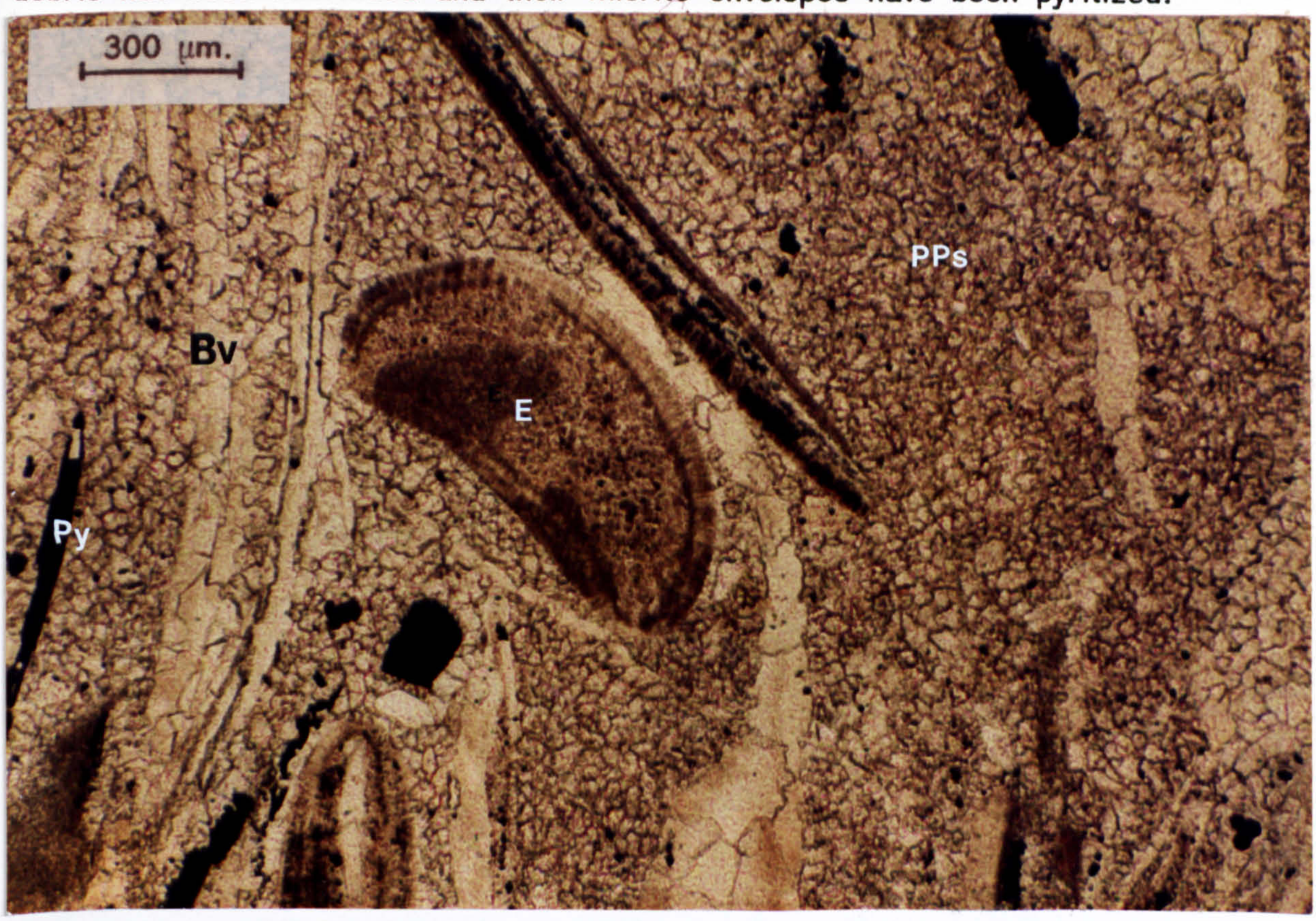


Plate 3.55. Recrystallized bioclastic packstone (p.p.l.).
Recrystallized bivalves (RB) with remnant pyritized micrite envelopes (ME) in a recrystallized, non-ferroan calcareous matrix from Wainlode 12. Remnant micrite patches (M) are present within the recrystallized pore filling calcite.

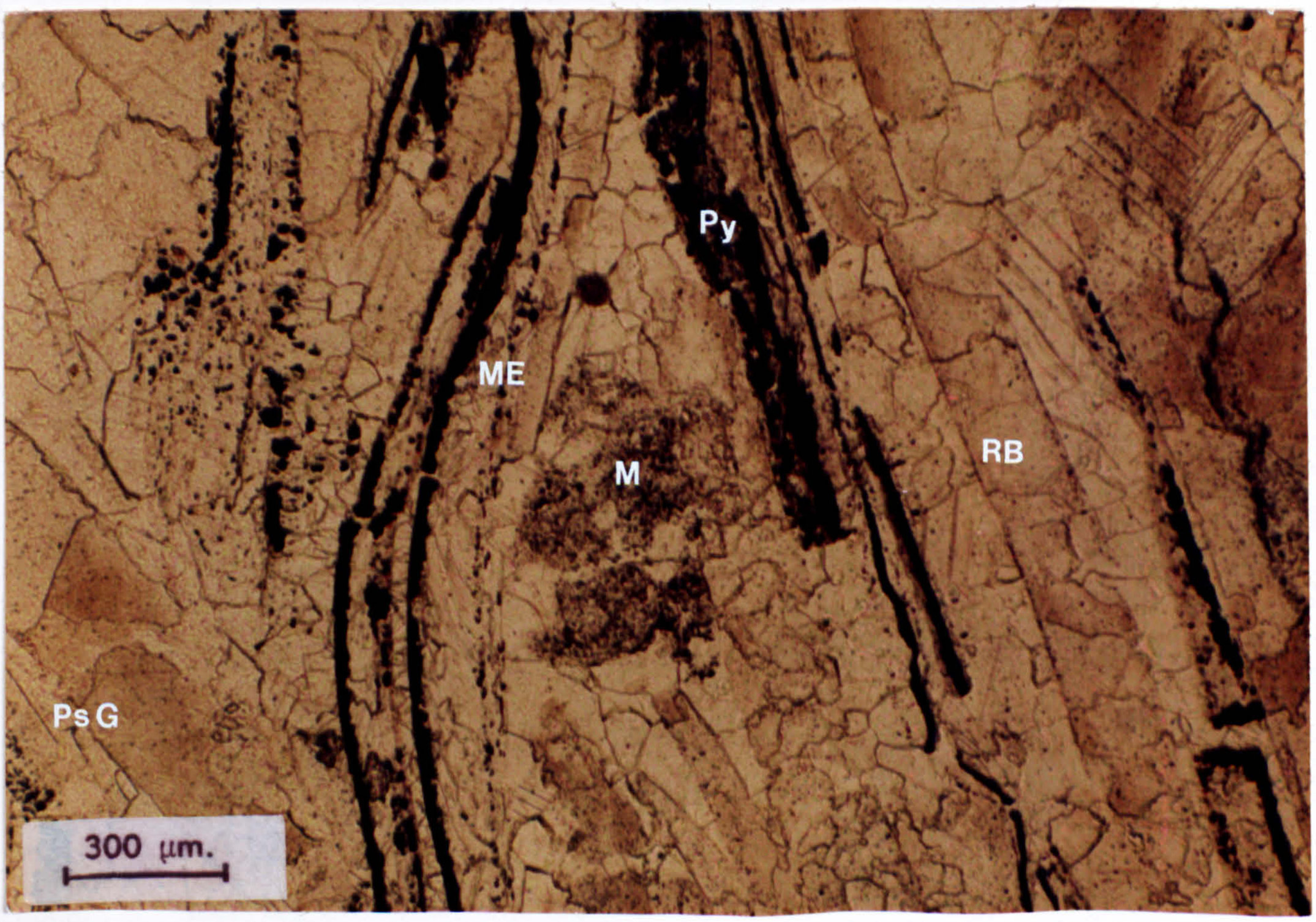


Plate 3.56. Fibrous calcite on top surface of bioclastic packstone. Cone-in-cone calcite (C-C) on top of bioclastic packstone (BPst), from Penarth 13.

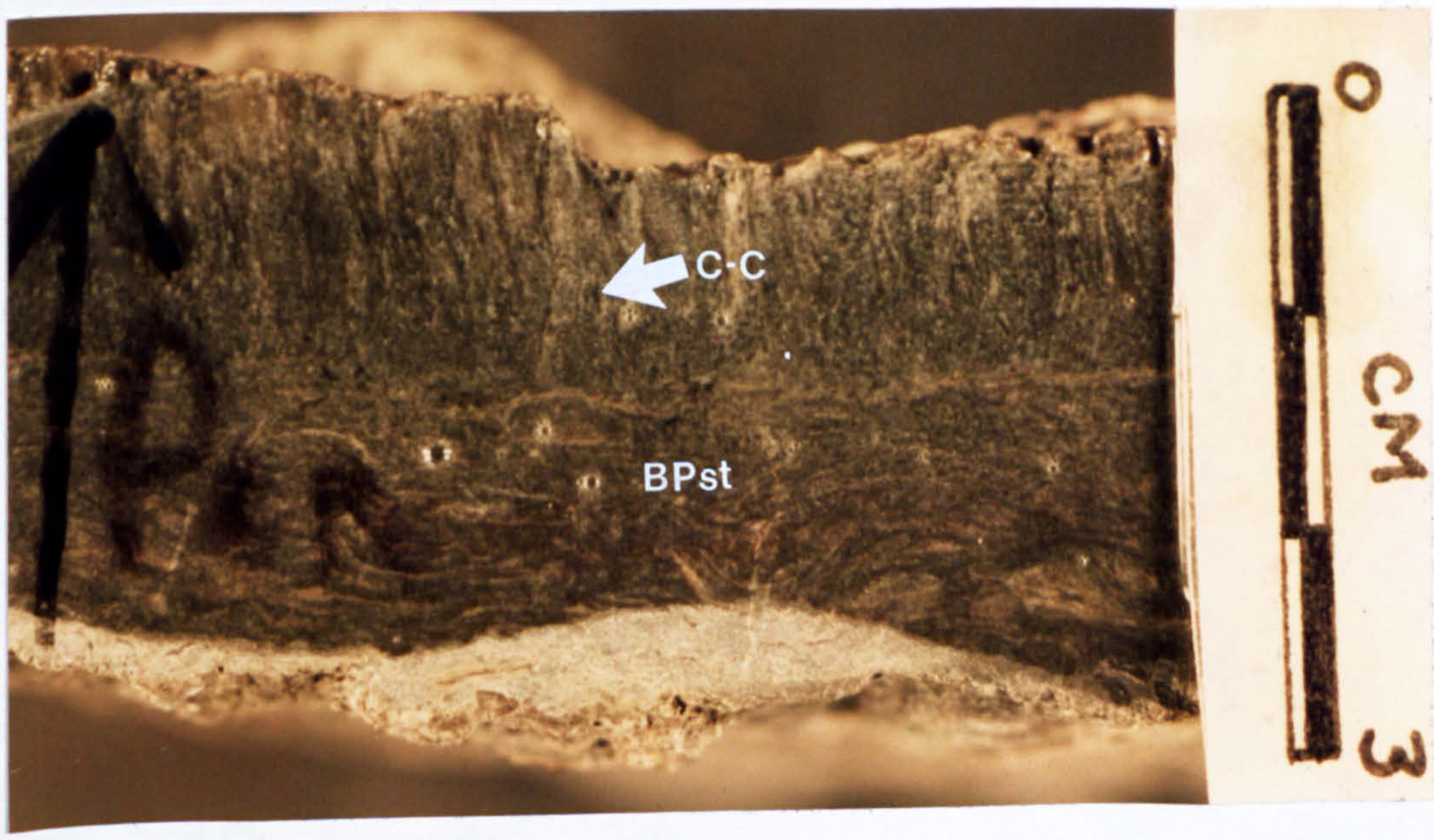
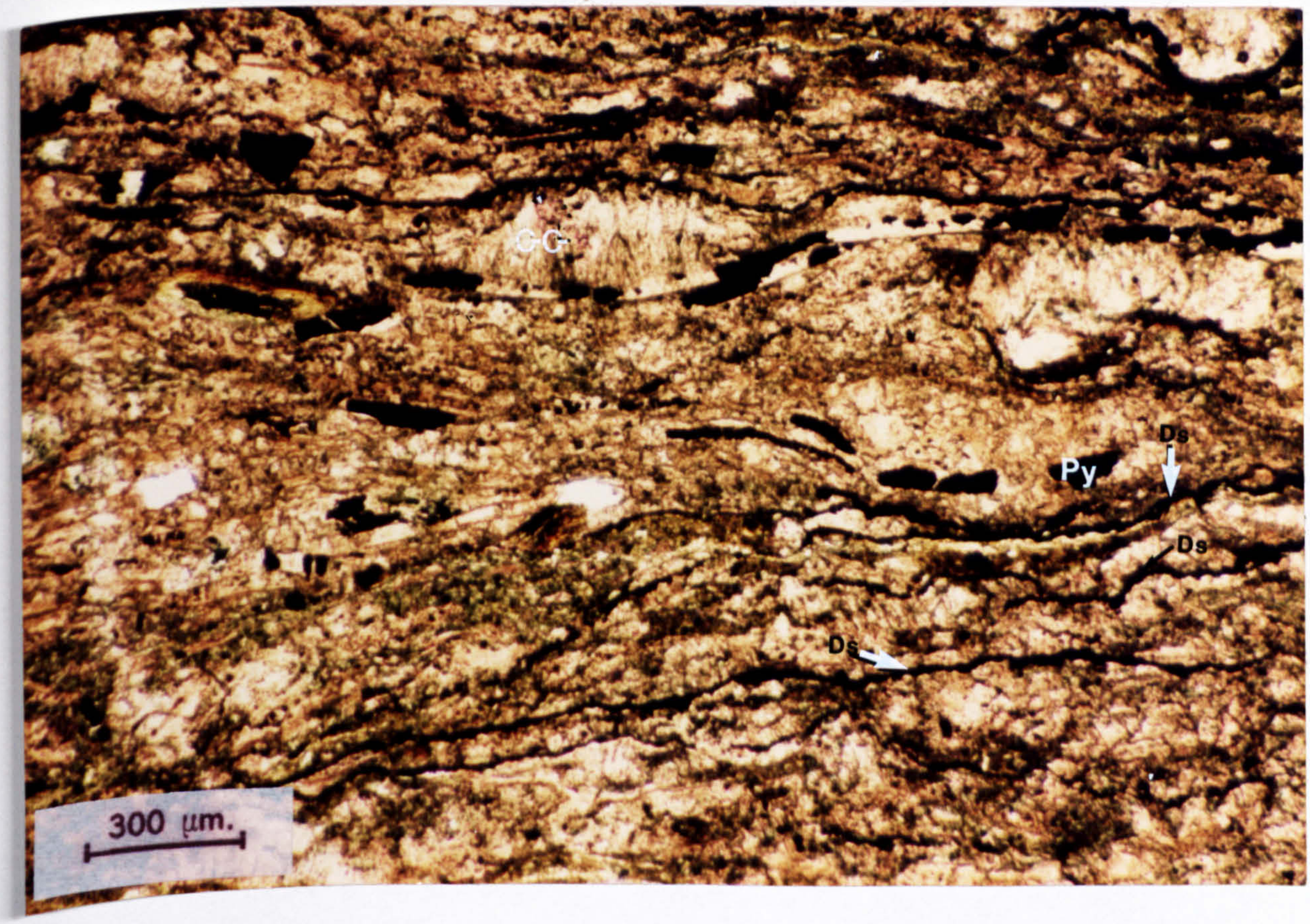


Plate 3.57. Fibrous calcite growing on packstone (p.p.l.). Non-ferroan, fibrous cone-in-cone calcites (C-C), with included pyrite framboids (Py) growing within an intensely recrystallized bivalve (Bv) rich packstone, from Penarth 11. Only the bivalves with micrite envelopes have a recognisable structure.

Plate 3.58. Intensely recrystallized bioclastic packstone (p.p.l.). Recrystallized and pyritized bivalves in a matrix of recrystallized inclusion rich calcite spar, with fibrous calcite (C-C) from Carrefour 13. The fibrous calcites appear to be seeded upon the bivalve fragments and are associated with dissolution seams and clay concentrates (DS).



Section 3.4b. Facies interpretation.

The presence of facies couplets with disarticulated, convex-up bivalve debris and rare end-on fabrics, mud drapes and mud geopetals suggests that deposition occured in fluctuating energy conditions (after Specht and Brenner 1979), as a consequence of storms (after Kresia 1981). The helical currents generated by storm waves rework the coarser sediment fractions and place the finer fraction in suspension. This process stirs up the sediment, without transporting it far and supports some of the shells in an apparently unstable, end-on position (Bambach *et al.* 1978, Kresia 1981). Obviously once storm activity ceases and flow conditions return to "normal" the finer fractions settles out, and drapes and infiltrates the underlying coarser unit. Thereby forming the facies couplets, mud drapes, mud geopetals and mud infiltration fabrics, which overall are interpreted as "graded rhythmites" (after Kresia 1981 and Kresia and Bambach 1982).

Like the other Westbury Formation facies there is little evidence of continuous unidirectional current activity within the packstone units, as they are poorly sorted, unwinnowed (apart from the formation of the mud drapes) and generally lacking diagnostic current structures (of course this may in part be due to bioturbation, although burrowing has not disturbed the facies couplets and burrows have not been observed in these units).

The bivalve fragments often contain large flask shaped borings up to 400um. in diameter, which are interpreted as having been formed by sponges (after Bromley 1975). Partially pyritized micrite envelopes also surround much of the shelly material. These envelopes were probably formed by the boring activity of endolithic algae and fungi (Bathurst 1975) and subsequently pyritized when localized sulphate reducing conditions were produced as the endolithic organisms decayed. As some of the shells are intensely bored and the shells are still recognizable it is likely that the shells, after they had been bored, were not transported far as otherwise they would have broken-up.

Much of the biogenic debris has been sheathed by bright luminescing, continuous, tangential, non-ferroan calcite coats, which are interpreted as being cortoids (Fabricius 1977). Unfortunately their origin in the Westbury Formation is enigmatic. Modern coated grains are known to form as a consequence of both inorganic and organic process (Fabricius 1977 and Brand and Veizer 1983) and have been found forming in cyanobacterial (Cohen *et al.* 1975, Krumbein 1977, Krumbein 1979) and algal mats (Riding 1983). There is no evidence that either algal or cyanobacterial mats were present in these packstones, however algal lamination has been observed in the calcarenaceous sandstones (see section 3.3b), which suggests (assuming that they have a biological origin) that they were transported into the facies. A clue to their origin however lies in the fact that they are composed of non-ferroan, bright luminescing calcite; which either implies that they formed in sub-oxic conditions where there was Mn^{++} available but no Fe^{++} available to enter the calcite lattice, or in the sulphate reduction zone where Fe(II) was being preferentially incorporated into pyrite leaving the calcite Fe^{++} depleted but Mn^{++} enriched and thus non-ferroan and bright lumiescing (Carpenter and Oglesby 1976). Implying that they have a biological but are not now preserved *in-situ.*

Spherulites are preserved beneath some of the bivalve debris. They too probably have an algal or fungal origin (Fabricius 1977), however like the cortoids it is not entirely clear if they formed *in-situ* or where transported into the unit.

The origin of micrite within the packstones is uncertain. Modern aragonitic mud is thought to derive commonly from the breakdown of calcareous algae (e.g. *Halimeda sp.*), inorganic precipitates (whitings), physical erosion processes and as a consequence of bioerosion by hard substrate grazers (Flugel 1982). It has also been observed forming in anoxic cyanobacterial mats (Krumbein and Cohen 1977), around bacterial sheathes (Krumbein 1974), as a consequence of micro-organism decay (Berner 1969, Maurin and Noel 1977) and as the result of diurnal changes in algal metabolism

(Friedman and Forer 1982). To complicate matters further microsparry calcite is known to form early during the diagenesis of organic rich sediments, as a byproduct of the pore waters being supersaturated with respect to bicarbonate and Ca(II) ions as a result of anaerobic metabolic process (Curtis 1977). In this context it is not clear which or indeed if any of these processes formed the primary lime mud, although clearly bioerosion process were occurring and algal/cyanobacterial mats may have been present, at least on a basin scale. It is almost certain however where facies couplets and mud drapes occur that the lime mud had a sedimentary rather than a diagenetic origin, as it was clearly not cemented. Despite this however it cannot be discounted that diagenetic microsparry calcite was reworked by strongly erosive environmental conditions.

Diagenesis.

Again the earliest phase of diagenesis preserved within the packstones is the precipitation of euhedral K feldspar overgrowths on irregular detrital K feldspar grains. K feldspar formation requires alkaline conditions with high concentrations of SiO_2, Al^{3+} and particularly K^+ ions (Hower 1981). In this context it is likely that the ions (particularly K^+) for K feldspar precipitation were derived from the dissolution of detrital illites, rather than from the dissolution of K feldspars as the detrital cores of the feldspars appear not to be etched. One mechanism, which may well have occured, by which localized early alkaline conditions can be achieved is by microbiological sulphate reduction.

It is worth noting that the phosphates appear not to be zoned, thus in the packstones the phosphatic debris is considered to be detrital.

The zoned, pore filling calcite spars that surround some of these K feldspar overgrowths are interpreted as being cements. The earliest of these cements to precipitate (zone I) are unzoned, bright luminescing, non-ferroan calcareous spars and these are followed by multizoned (zone II), bright

luminescing, non-ferroan spars. These bright luminescing phases are probably Fe(II) depleted and thus were either deposited in oxic conditions, or in reducing, sulphidic conditions where the Fe(II) was being incorporated into pyrite. As pyrite is directly associated with these two initial cements it is likely that they were indeed precipitated in the sulphate reduction zone where pyrite was mopping up any Fe^{++} in the pore waters (after Curtis 1977), with the sulphide being produced by bacterially mediated sulphate reduction (Berner 1970, Berner 1984). It is worth noting that the ions for the calcite precipitation probably derived from organic matter oxidation or from dissolution of other carbonates (Irwin 1980, Curtis 1980 and Curtis 1983).

Locally some of the shell debris has been replaced by pyrite. Pyritic replacement of shells occurs initially where H_2S concentrations build up in the pore waters as a result of excess sulphate reduction. This occurs because the excess H_2S (gas) disassociates into its component ions and lowers the pore water pH's, causing calcite dissolution, and where Fe(II) is present pyrite precipitation in its place (Raiswell 1976).

The textural evidence suggests that the formation of K feldspar overgrowths preceded the formation of the calcite cements. As both were probably initiated by alkaline conditions associated with bacterial sulphate reduction, it is interesting to speculate why the K feldspars were precipitated before the calcite. In this context it was probably due to the availability of the different component ions, with K^+,SiO_2 and Al^{3+} being made available earlier, as a result of the dissolution of detrital metastable clays, than the Ca^{2+} ions, which were presumably derived later by the dissolution of metastable carbonates. The earlier dissolution of the unstable detrital clays may have been due to their relatively increased surface area.

Ferroan, dull luminescing (zone III) calcite cements finally infilled the shelter porosity. These cements were clearly formed in reducing conditions where Fe(II) was available and not being incorporated into pyrite. In the post

sulphate reduction environment, reducing conditions are initially produced by methanogenic bacteria (Curtis 1980). Methanogens oxidize the organic matter which increases the pore water bicarbonate concentrations, and use organic molecules as electron acceptors (as no other inorganic oxidizing agents are present). The excess bicarbonate may then cause calcite cement precipitation (Irwin 1980), and if Fe^{2+} is still available in the pore waters a ferroan cement will form. Thus bacterially mediated methanogenesis probably caused at least some of the late stage ferroan cements to precipitate. It is also worth noting that thermal decarboxylation of the organic matter during burial might also supply the bicarbonate for ferroan cement precipitation (Curtis 1977).

Not all the primary porosity, even that which is closely spaced, is filled with a complete cement sequence. This implies that different microenvironments existed in the sediment, even within closely juxtaposed pores, implying that the sediment quickly became a closed system with respect to pore water migration.

Cements are not preserved where the micrite has recrystallized to non-ferroan calcareous pseudospar. This implies that at least some recrystallization post dated cementation. However it also clear that recrystallization of the originally aragonitic bivalve debris to pseudopleochroic non-ferroan calcite may have been a much earlier process (as shells with pseudopleochroic textures are preserved with cements). Recrystallization of metastable carbonates is caused by either a lack of Mg(II) ions (Folk 1974) or the presence of dissolved sulphides (Bathurst 1975). In this case the early recrystallization of the aragonitic shelly material was probably a consequence of the high concentrations of dissolved sulphides produced as a byproduct of bacterial sulphate reduction. Whilst the later recrystallization event (or events) that are cement destructive may have either occurred coupled with kerogen maturation, or as a consequence of shale dewatering releasing Mg^{2+} depleted pore water. It is worth noting that there is very little evidence of an Mg(II) rich authigenic phase e.g. chlorite, implying limited Mg^{2+} ion activity. Recrystallization may therefore have been caused by a number of processes and it is not clear which mechanism was dominant.

Vein displacive non-ferroan, dull luminescing calcites overgrow all the earlier diagenetic textures and often grow internally on dissolution seams. The partial dissolution of any remaining metastable carbonates in these units probably supplied the ions for their growth and caused the destruction of the earlier fabrics. As these vein displacive calcites grew they incorporated previously formed pyrite framboids into their structure. The fact that the calcites are composed of dull luminescing, non-ferroan calcite implies that they contain neither activator or quencher ions. As they formed after the methanogenic zone and probably in reducing conditions then this presents a problem. In order to reconcile these facts it is assumed that either these vein dispacive calcites formed in Fe(II) or Mn(II) depleted conditions, or they grew slowly enough to exclude the contaminant ions.

A summary of the sedimentological and diagenetic events is presented in figure 3.8.

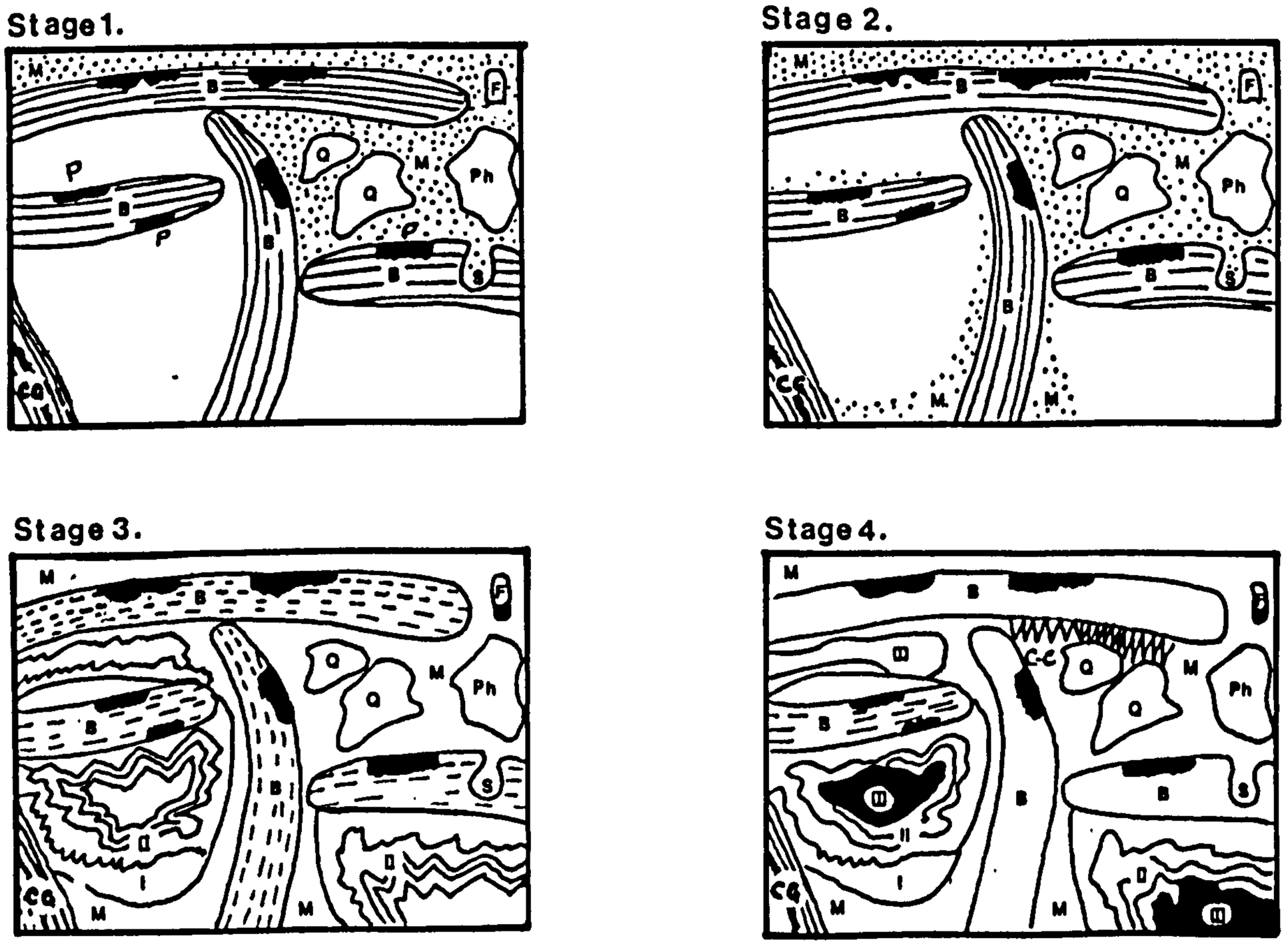
Figure 3.8.

Stage 1, Marine phreatic with low/no porewater oxygen, just post storm. Deposition of detrital quartz (Q), reworked bivalves (B) (with sponge borings (S) and pyritized micrite envelopes (P)), K feldspar (F), coated grains (CG) and phosphate (Ph) with the primary porosity being partially infilled with calcareous mud (M) which drapes the coarser biogenic fragments.

Stage 2, Marine phreatic, with low/no dissolved pore water oxygen, post storm. The fine fraction settles out and the carbonate mud infiltrates the shelter porosity forming the mud geopetals.

Stage 3, Sulphate reduction zone, alkaline, reducing pore waters, early burial. Cementation of the carbonate mud and precipitation of the K feldspar on the detrital K feldspar cores. Precipitation of non-ferroan, bright luminescing zone I and zone II calcites and recrystallization of the bivalve debris.

Stage 4, Methanogenic/post methanogenic zone, alkaline, reducing pore waters. Precipitation of ferroan, zone III calcite, formation of fibrous calcites (C-C) and replacement of some of the bivalve debris with ferroan calcite as a consequence of shale dewatering in an iron limiting environment.



Section 3.5a. Wackestones.

Nodular bioclastic wackestone units are present in the Westbury Formation (plate 3.69). They contain rare, scattered, partially pyritized, uncrushed bivalves, gastropods and echinoderm debris in a microspar matrix (plate 3.59, plate 3.60 and plate 3.61). They also have a minor siliceous component comprising: (<1% K feldspar, quartz and < 2um. clays (illite and kaolinite). The wackestone units have no visible depositional fabrics. Sparry (occasionally multizoned) calcites are preserved in mouldic and shelter porosity, beneath and around the bivalves and within the gastropods (plate 3.59, plate 3.60 and plate 3.62). The microspar and most of the pore lining calcite spars are composed of non-ferroan, bright luminescing, zone I and zone II calcite (plate 3.62), whilst the biogenic debris and a small proportion of the calcareous spars are composed of ferroan, non-luminescing zone III calcite (plate 3.61 and plate 3.62).

The wackestone units have often been fractured, and the resulting cracks have been infilled with non-ferroan (bright luminescing), type I and ferroan non (luminescing) type III calcite spar (plate 3.63).

At some localities the microspar has recrystallized to bright luminescing pseudosparry calcite whilst elsewhere it has been replaced by pyrite (plate 3.64).

Plate 3.59. Bioclastic wackestone (p.p.l.).
Gastropod (G) in a matrix of non-ferroan calcareous microsparry calcite (M), from St. Audries 5. The shelter porosity within the gastropod whorls is infilled with non-ferroan microsparry calcite (Ms) and non-ferroan sparry calcite (NFC).

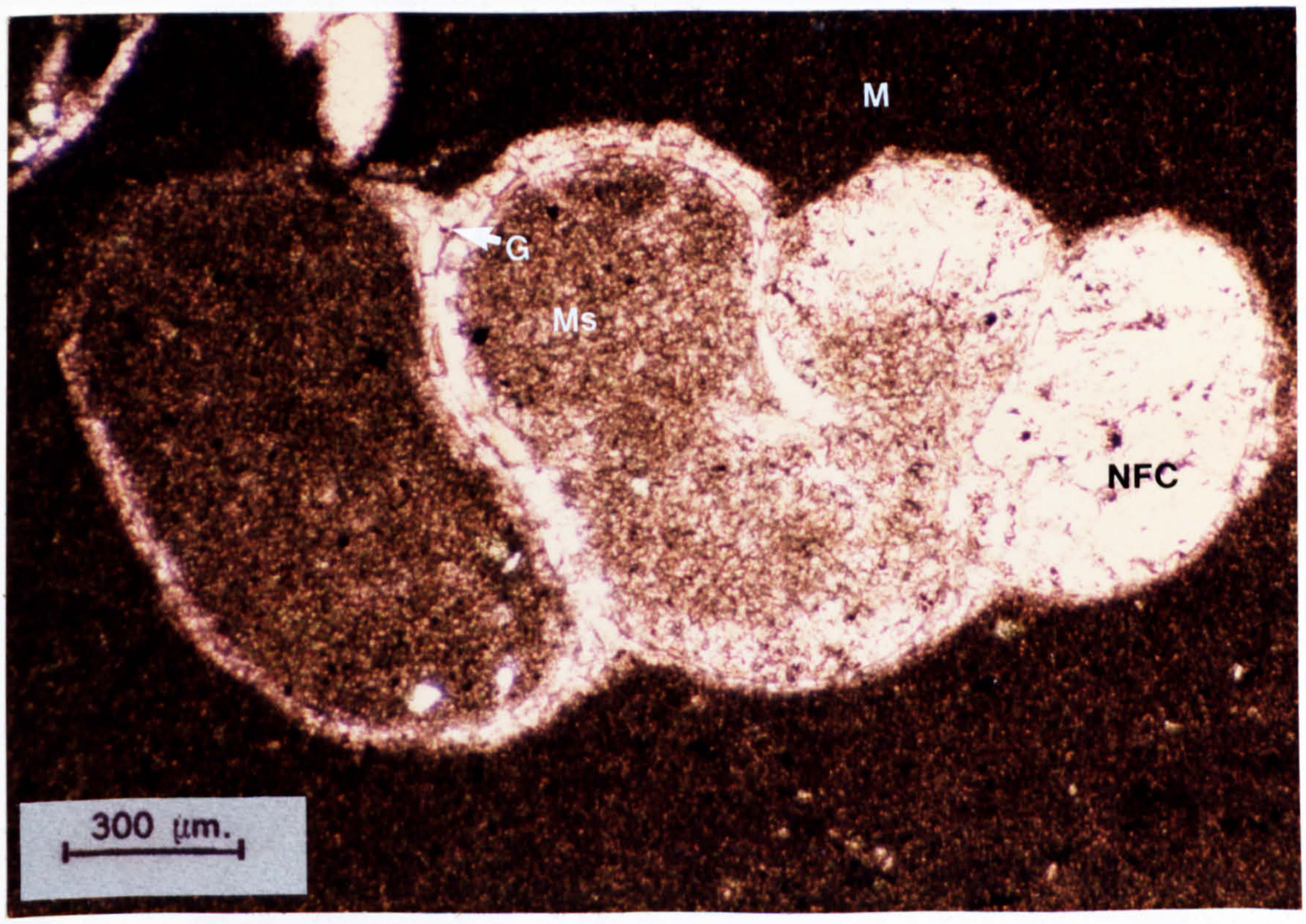


Plate 3.60. Bioclastic wackestone (p.p.l.).
Recrystallized bivalve debris in a matrix of non-ferroan microsparry calcite (M), from Lavernock 41. Early mouldic porosity has formed prior to the cement infill of the shelter porosity within the bivalve cavity, as the same cement sequence of early acicular calcite (1) followed by sparry non-ferroan calcite (NFC2) exists both inside and outside the bivalve.

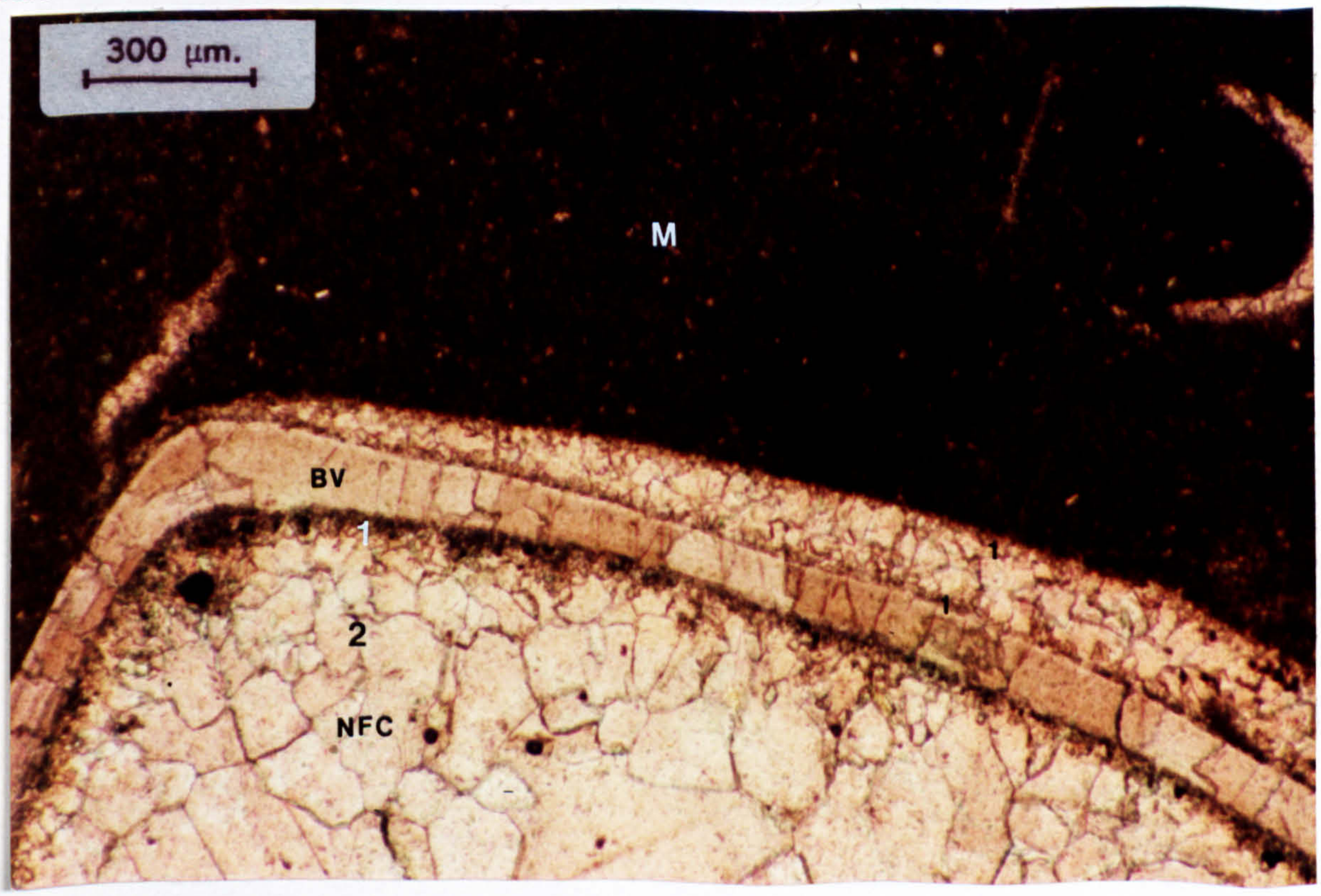


Plate 3.61. Bioclastic wackestone (CL.).
Recrystallized, dull luminescing bivalves (Bv) in a matrix of bright luminescing microsparry calcite (Ms), from Penarth 11. Rare, dull luminescing echinoderm plates (E) are also present, which are coated in a bright luminescing early sparry calcite. The bivalve debris contains small flask shaped borings (arrowed).

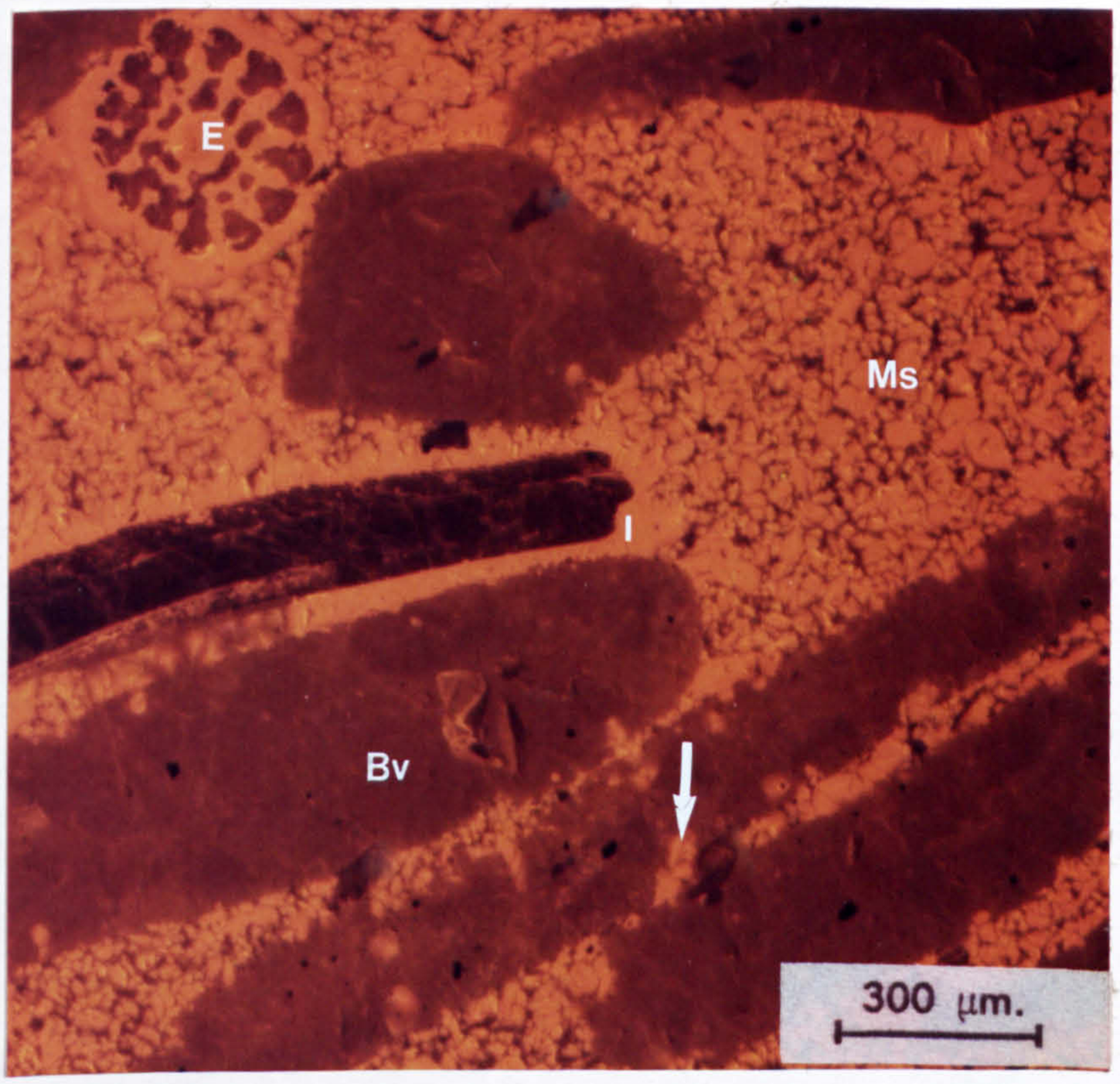


Plate 3.62. Bioclastic wackestone (CL.).
Dull luminescing gastropod (G), with zoned cement infill in a matrix of bright luminescing microsparry calcite, from St. Audries 5. At least two cement zones are present within the shelter porosity (inside the gastropod whorl) - zone I bright luminescing unzoned calcites (I) and zone II multizoned bright luminescing calcites (II).

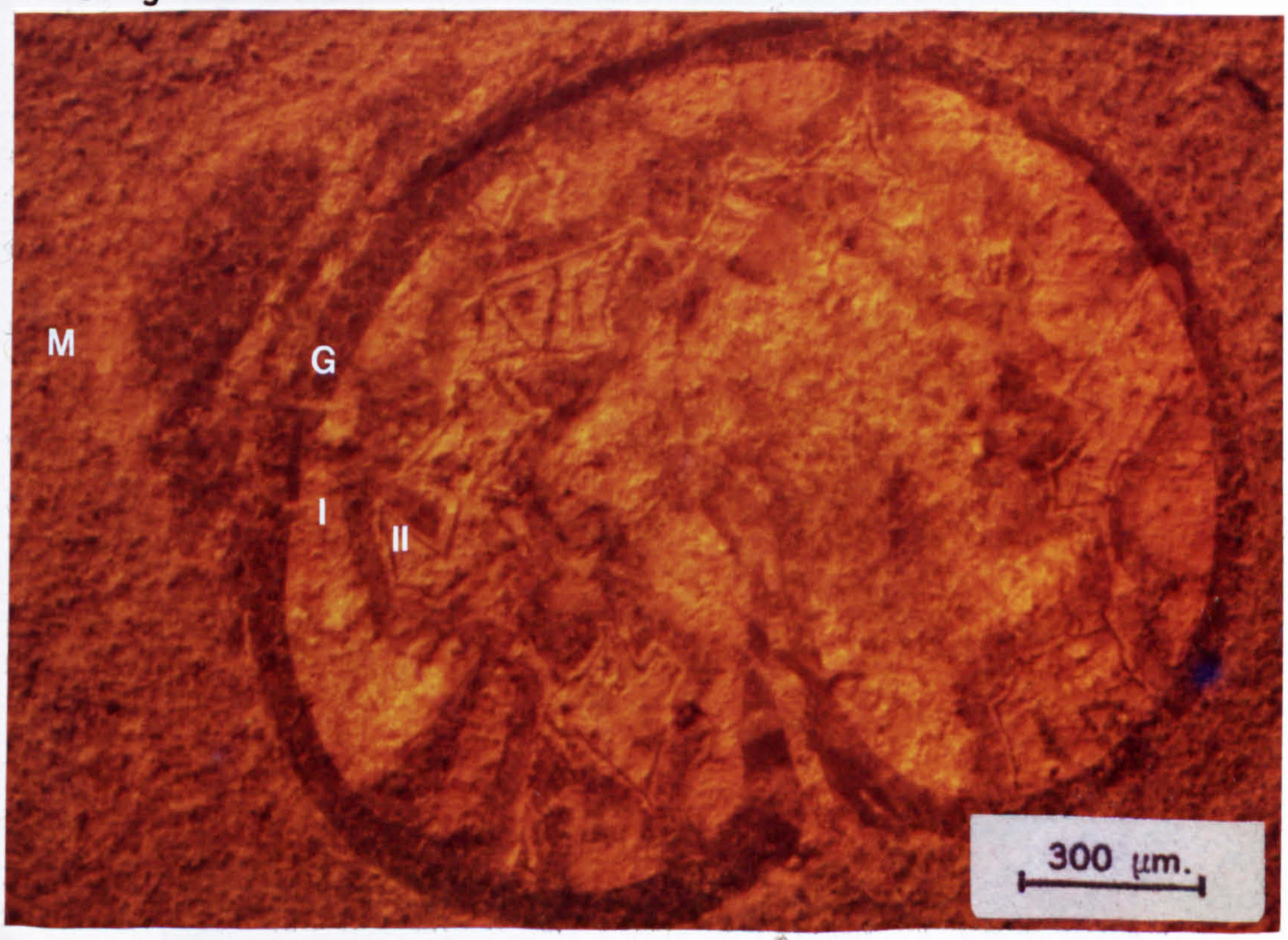


Plate 3.63. Bioclastic wackestone (CL.).
Fractured, dull luminescing bivalve fragments (Bv) in a matrix of bright luminescing microsparry calcite (M), from Penarth 11. Post initial cementation the unit has been fractured and the resulting fracture porosity has been infilled initially by bright luminescing zone I spars (I) and latterly by dull luminescing zone III sparry calcites (III).

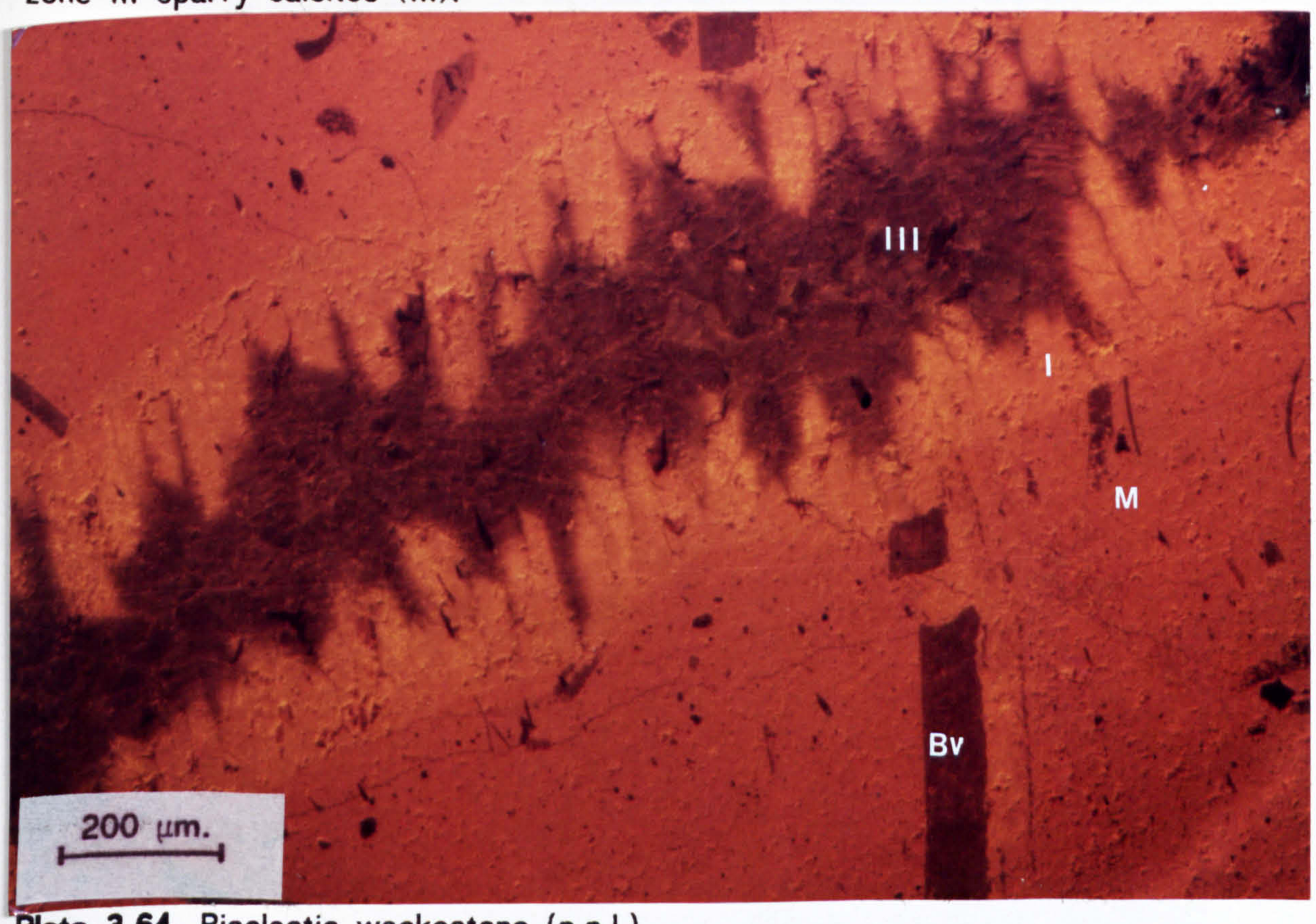
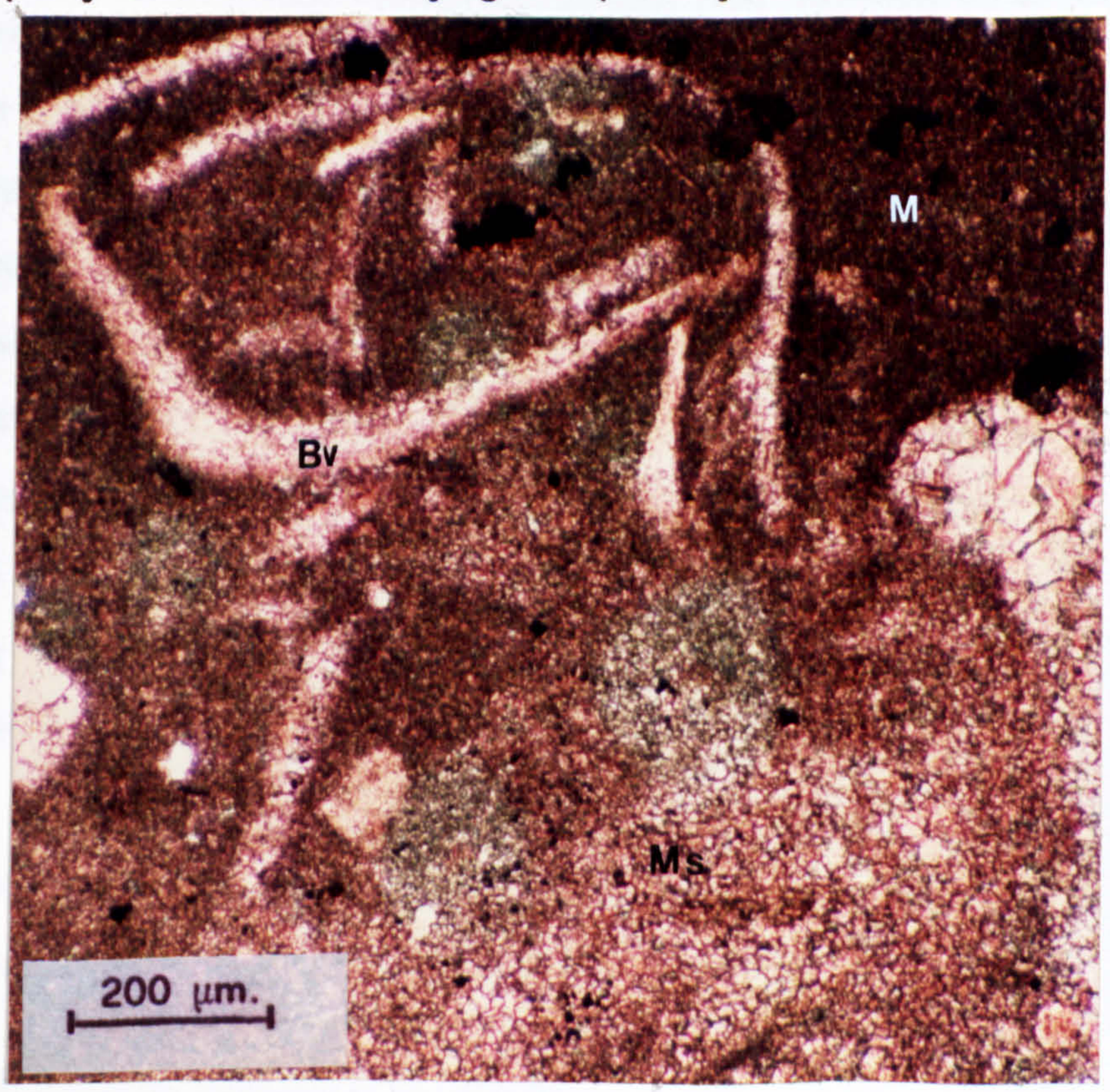


Plate 3.64. Bioclastic wackestone (p.p.l.).
Recrystallized bivalves (Bv) in a matrix of non-ferroan microsparry (M) and recrystallizing microsparry calcite (Ms), from Penarth 11. Recrystallization of the microsparry calcite is destroying the primary textures.



Section 3.5b. Facies interpretation.

These nodular wackestones almost certainly precipitated displacively into uncompacted sediments (Raiswell 1976 and Irwin 1980), rather than as a consequence of lime mud sedimentation, as they contain:- cements characteristic of bacterially mediated diagenetic processes (see below), are unbioturbated, contain no depositional fabrics (of course intense bioturbation may have destroyed these textures) and the surrounding mudstones have compacted around them. The microsparry matrix is composed of non-ferroan, bright luminescing calcite which in the context of an alternating organic mudstone/wackestone sedimentary sequence, was probably precipitated in the sulphate reduction zone. In this zone the excess Fe(II) is mopped up by the sulphides to form pyrite; and the increased alkalinity associated with Fe(III) reduction, coupled with the pore waters being supersaturated with respect to bicarbonate (as a consequence of the oxidation of the organic matter), localized non-ferroan calcite cement precipitation occurs (Curtis 1980).

In mudrocks microsparry calcite cements precipitate in preference to sparry calcites, because there are many potential nucleation sites. Sparry cements only precipitate where there are limited nucleation sites, which in this context was within the shelter and mouldic porosity associated with calcareous fossils. This primary porosity was initially infilled with bright luminescing, non-ferroan, zone I and zone II calcite spars and latterly by dull luminescing, ferroan, zone III calcite spars. This cement sequence was almost certainly precipitated as a consequence of anoxic oxidation of the organic matter initially by sulphate reducers and latterly by methanogens or by decarboxylation processes during later burial. While there is no pyrite directly associated with the sulphate reduction cements, it is present in the surrounding mudstones and thus would act as an efficient sink for Fe(II), consequently the absence of early ferroan cements is unsurprising.

During early burial some of the cemented wackestone units were fractured and the resulting fracture porosity was infilled with early, bright

luminescing zone I cements (which presumably have a sulphate reduction origin) and later dull luminescing ferroan cements (with a methanogenic or decarboxylation origin). Consequently fracturing must have been a very early process, occuring within a few metres of the sediment water interface.

Locally the microspar has recrystallized to pseudospar and the primary textures obscured. This recrystallization was almost certainly a consequence of the pore waters being out of equilibrium with the microspar - Bathurst speculated that this may have either been due to a lack of Mg(II) ions or an excess of H_2S (Bathurst 1975). As the non-ferroan calcite cements have definitive sulphate reduction characteristics it is likely that recrystallization was post sulphate reduction and thus a fairly late stage process. In the light of this and the absence of conclusive evidence it is proposed that recrystallization in the wackestone facies was caused by deeper dewatering processes possibly associated with burial, where the formation waters were out of equilibrium with the microspar.

The diagenetic history is summarized in figure 3.9.

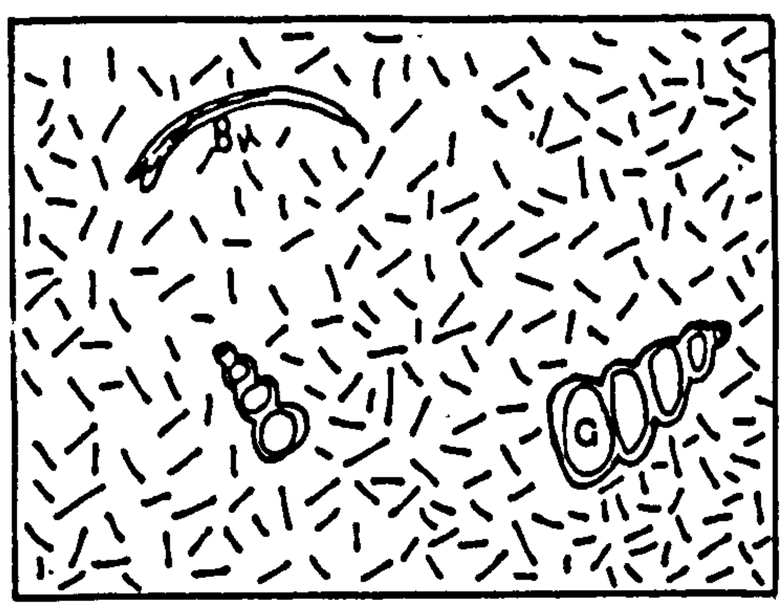
Figure 3.9.

Stage 1, Marine phreatic, anoxic, reducing bottom waters.
Deposition of anoxic organic rich muds, with rare mollusc debris (Gastropods (G) and bivalves (B)).

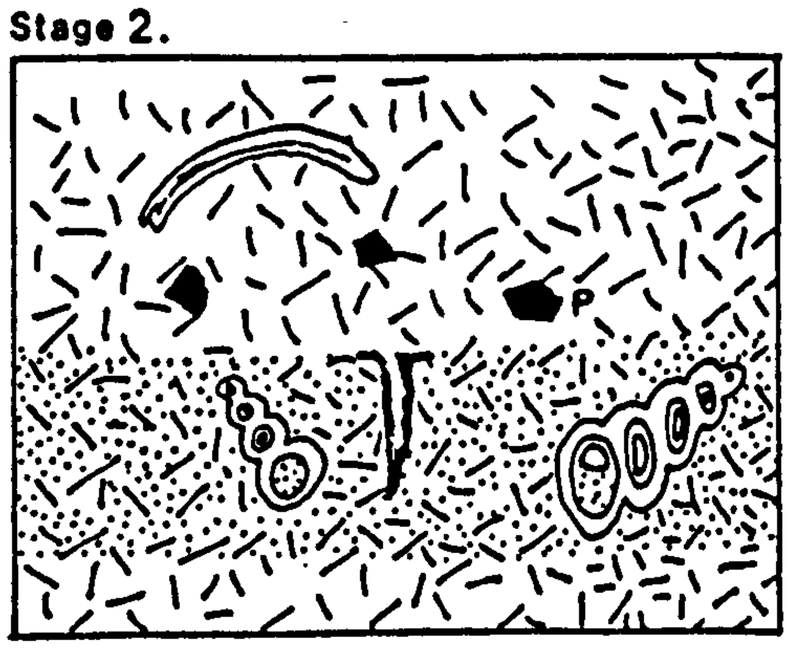
Stage 2, Sulphate reduction zone, anoxic, sulphidic porewaters.
Localized precipitation of non-ferroan microsparry calcite as a consequence of the porewater being supersaturated with respect to bicarbonate and alkaline as a result of Fe(III) reduction. Precipitation of pyrite in the adjacent shales. Fracturing of the microsparry unit.

Stage 3, Methanogenic/thermal decarboxyaltion zone, anoxic non-sulphidic porewater.
Compaction and dewatering of the mud around the cemented horizon. Recrystallization of microsparry calcite to pseudospar and replacement of gastropod shell with zone III calcite, as a consequence of the pore waters being out of equilibrium with the formation water. Precipitation of zone III ferroan calcite in the fracture porosity.

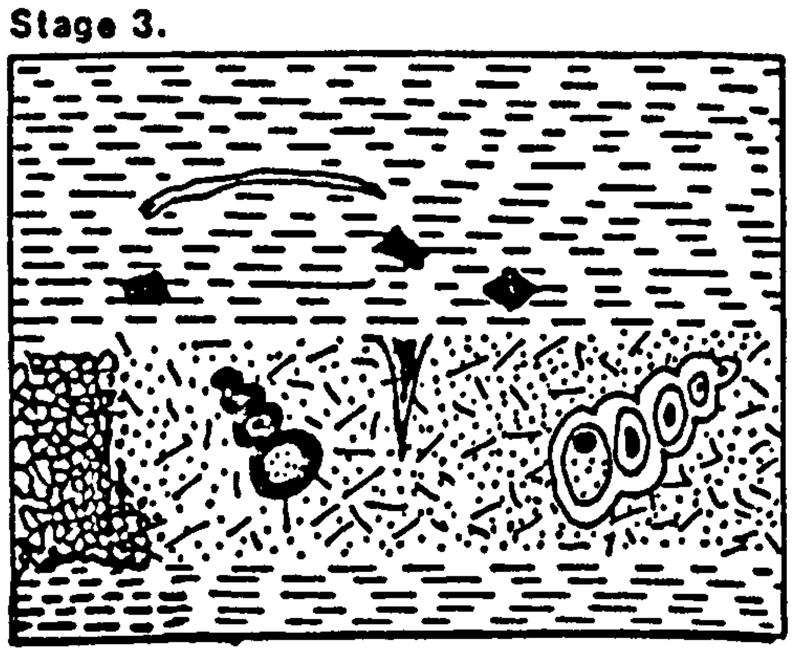
Stage 1.



Stage 2.



Stage 3.



Section 3.6a. Mudstones.

Black, fissile mudstones are a common component of the Westbury Formation (plate 3.75), they are composed of silt grade quartz, K feldspar and contain an illite-kaolinite clay assemblage (figure 3.10). They are very pyritiferous and may contain up to 10% organic matter (plate 3.66). Locally, notably at Upton, they also contain a "mixed-layer" illite/smectite mineral suite (figure 3.10). These organic-rich mudstones are unbioturbated and show no evidence of current activity. Generally they contain no macrofossils.

The organic matter is dominated by the presence of odd numbered acyclic n-alkanes (figure 3.11, figure 3.12 and figure 3.13), isoprenoids (figure 3.11, figure 3.12 and figure 3.13), steranes (figure 3.14 and figure 3.18, summarized in figure 3.19), diasteranes (figure 3.15), 4-methyldiasterenes (figure 3.16) 4-methylsteroidal (figure 3.14) and hopanoid (figure 3.17) components (which are summarized in table 3.1).

Figure 3.10. X-ray spectra of the untreated, glycolated and heated <2um fraction, from Upton 9. The dominant clays are illite (I), kaolinite (K) and an illite/smectite(I/S) "mixed-layer" phase. Glycolation has caused the expansion of the d-spacing and thus a move to lower two theta values in the illite/smectite phase, and heating has caused the kaolinite and illite/smectite peaks to collapse.

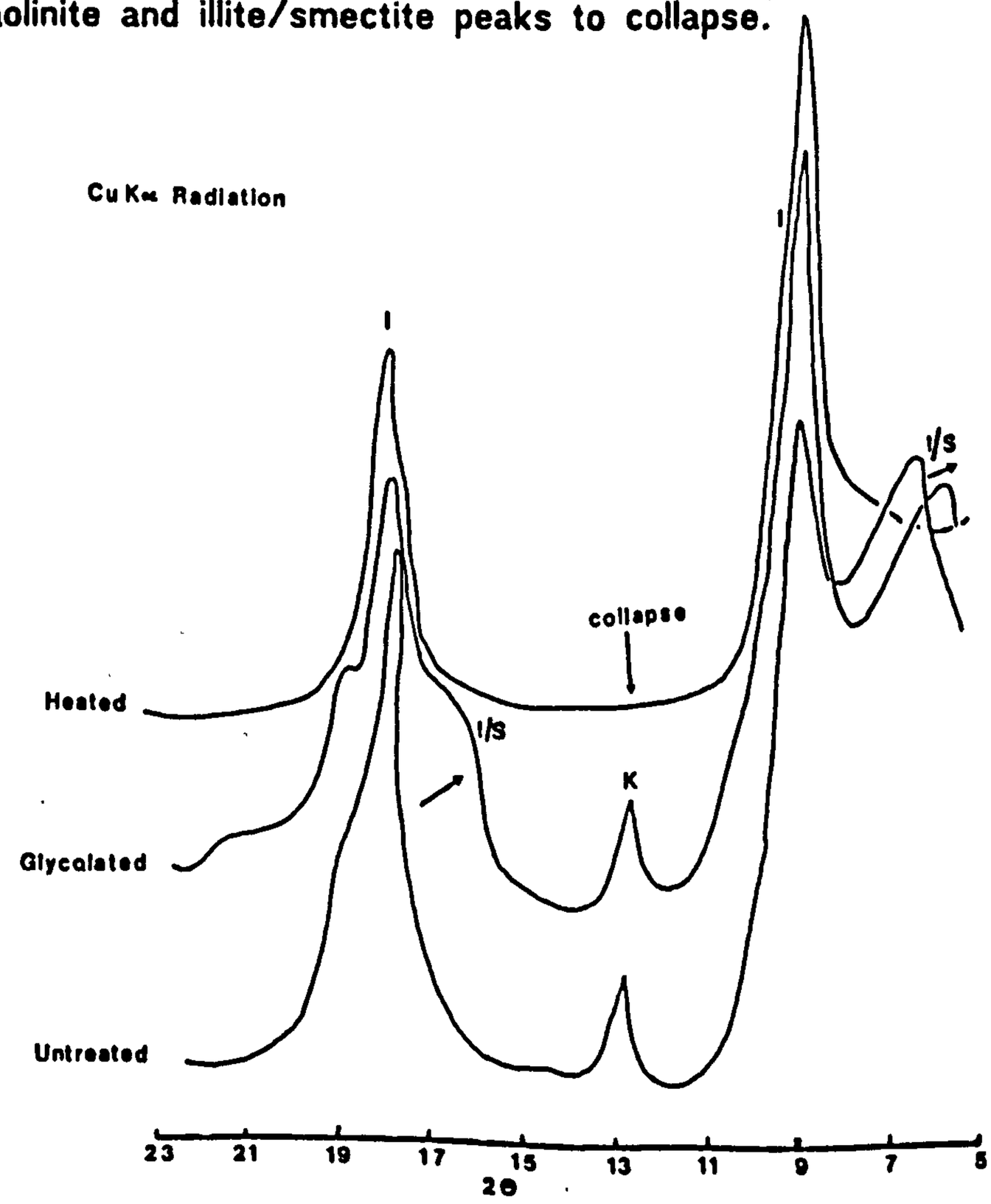


Figure 3.11. (a) Aust Cliff (b) Penarth. Partial mass fragmentograms of m/z 85 and reconstructed ion chromatogram (RIC), which are characteristic of n-alkanes (numbers designating different homologues) and acylic isoprenoids 16i (2,6,10-trimethyltridecane), 18i (2,6,10-trimethylpentadecane), Pr (pristane) and Ph (Phytane).

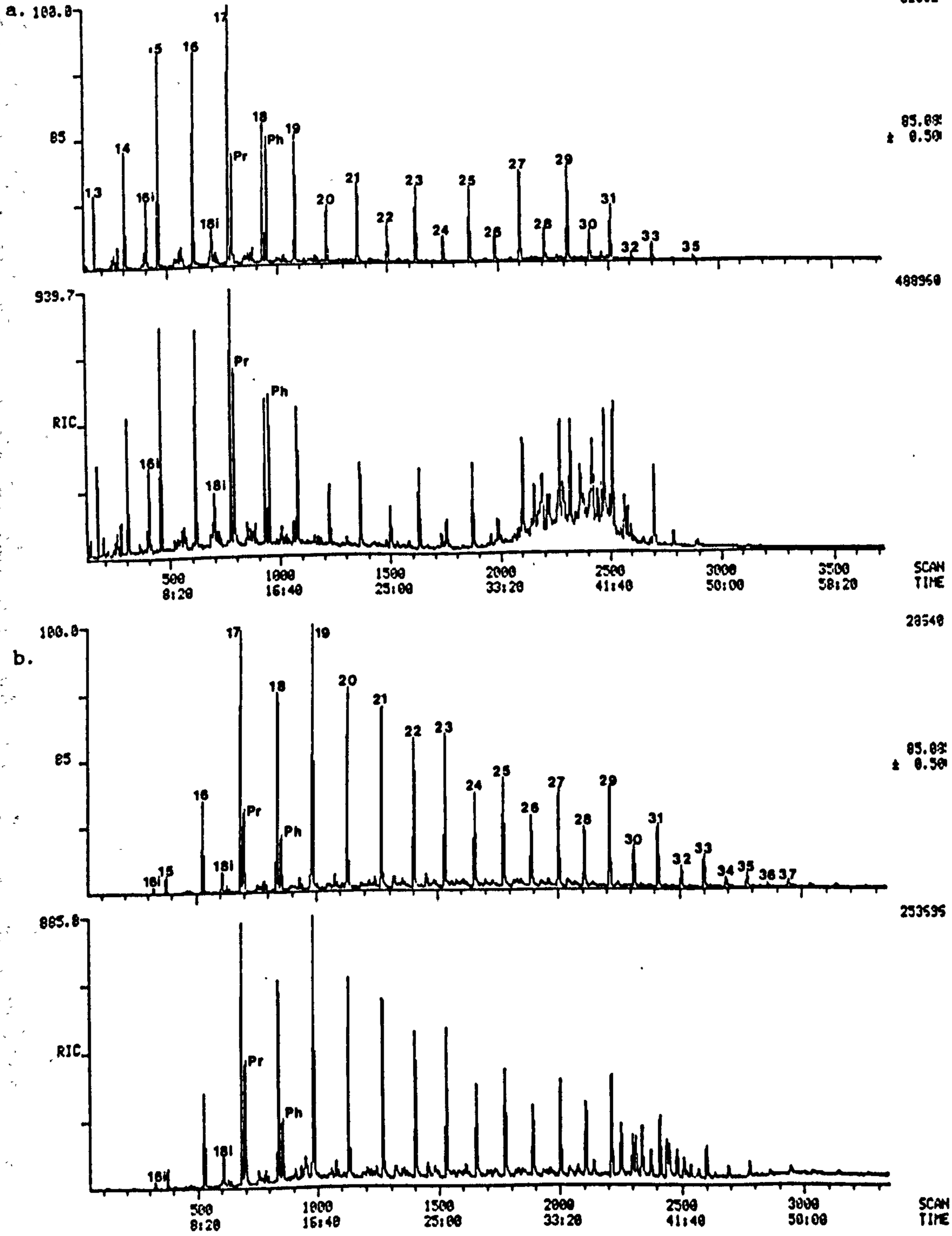


Figure 3.12. (a) Westbury-on-Severn (b) Stowell Park. Partial mass fragmentograms of m/z 85 and reconstructed ion chromatogram (RIC), which are characteristic of n-alkanes (numbers designating different homologues) and acylic isoprenoids 16i (2,6,10-trimethyltridecane), 18i (2,6,10-trimethylpentadecane), Pr (pristane) and Ph (Phytane).

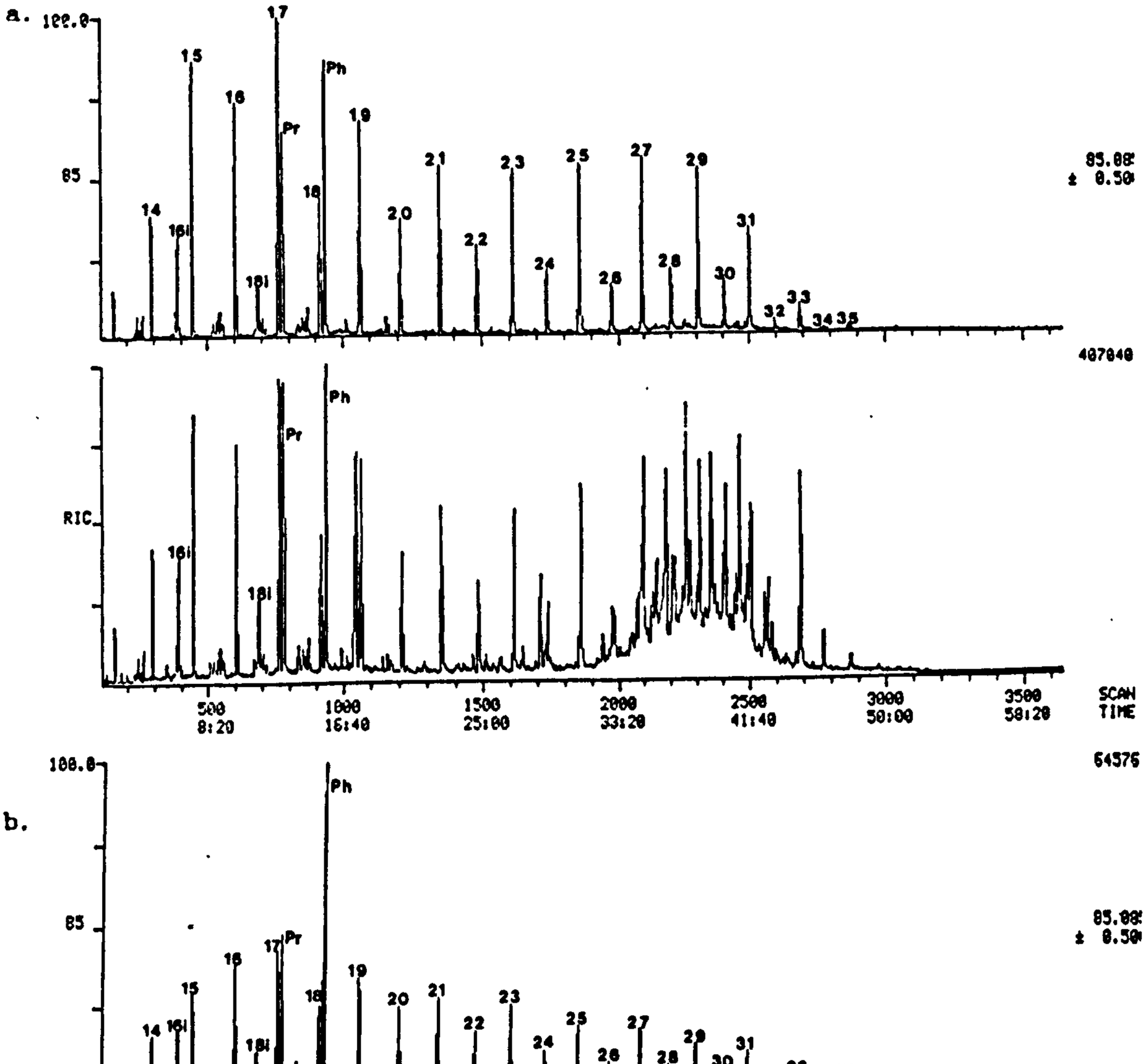


Figure 3.13. (a) Burton Row (b) Watchet Harbour. Partial mass fragmentograms of m/z 85 and reconstructed ion chromatogram (RIC), which are characteristic of n-alkanes (numbers designating different homologues) and acylic isoprenoids 16i (2,6,10-trimethyltridecane), 18i (2,6,10-trimethylpentadecane), Pr (pristane) and Ph (Phytane).

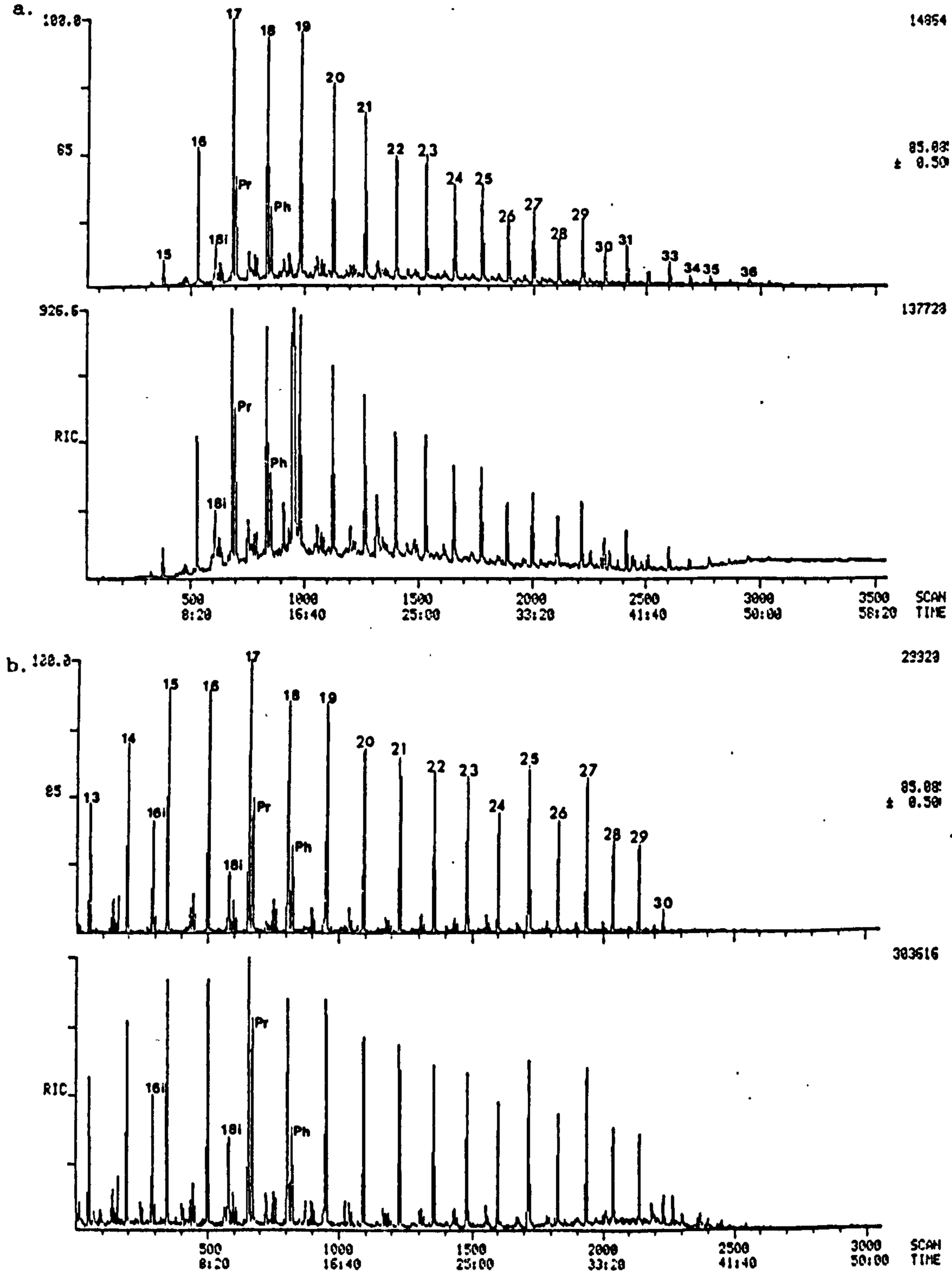


Figure 3.14. (a) Aust Cliff, (b) Burton Row. Partial mass fragmentograms of m/z 217, m/z 372, m/z 386 and m/z 400 illustrating the distribution of steroidal homologues.

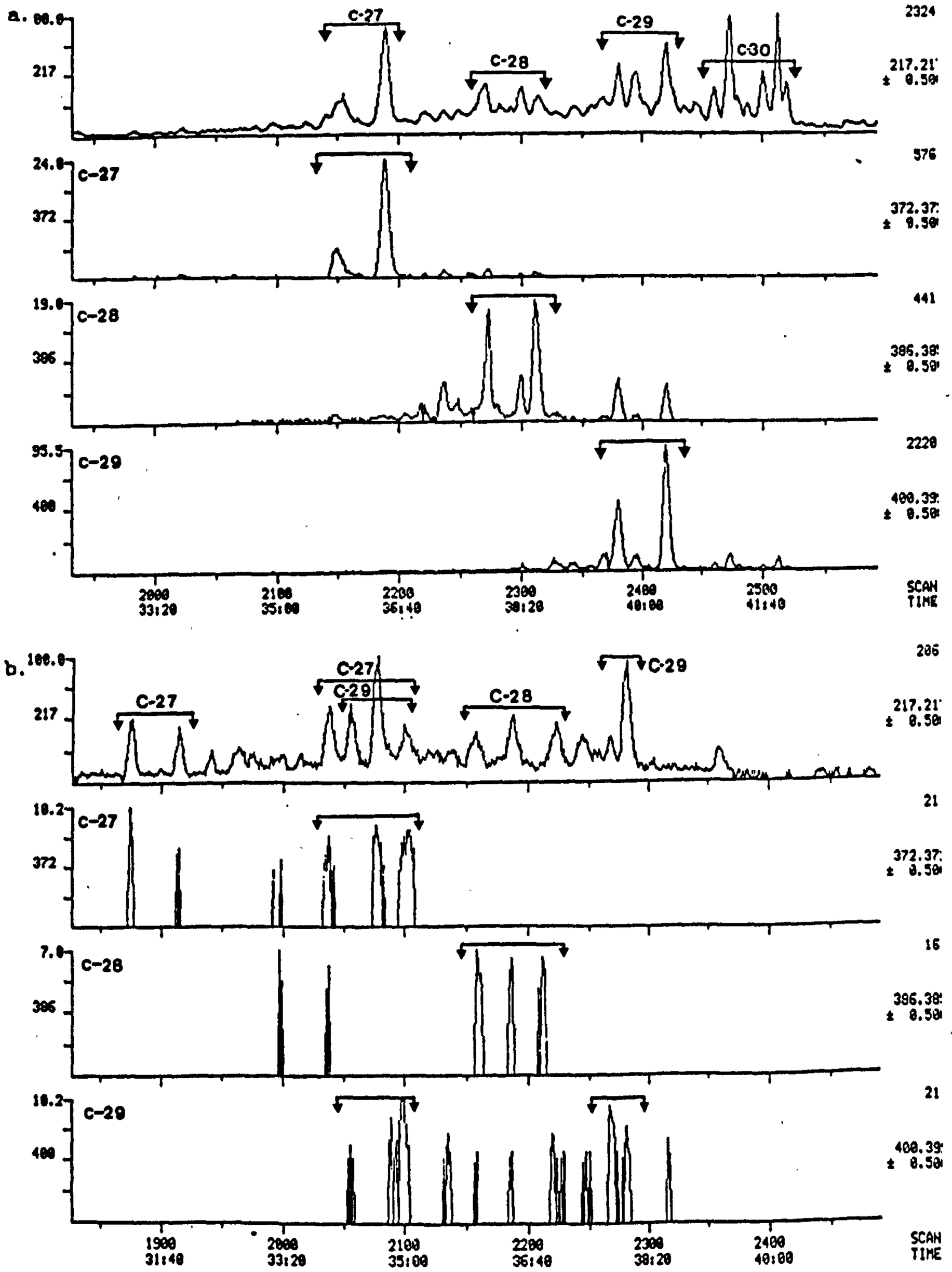


Figure 3.15. Westbury-on-Severn (b) Watchet Harbour. Partial mass fragmentograms of m/z 257 and m/z 259 illustrating the distribution of diasterenes and diasteranes, with the numbers illustrating the different homologues.

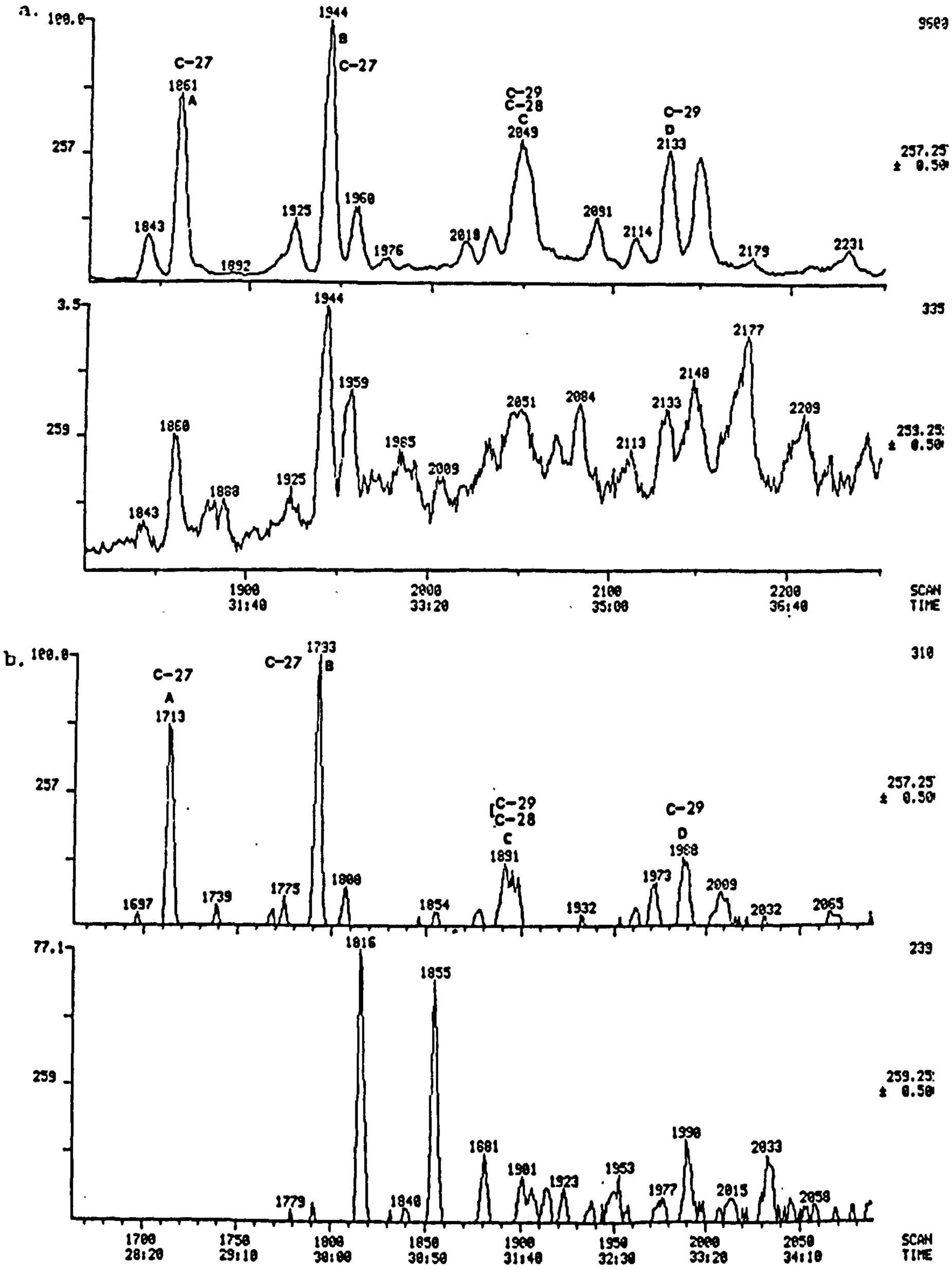


Figure 3.16. Westbury-on-Severn (b) Watchet Harbour. Partial mass fragmentograms of m/z 257 and m/z 271 illustrating the distribution of diasterenes and 4-methyldiasterenes.

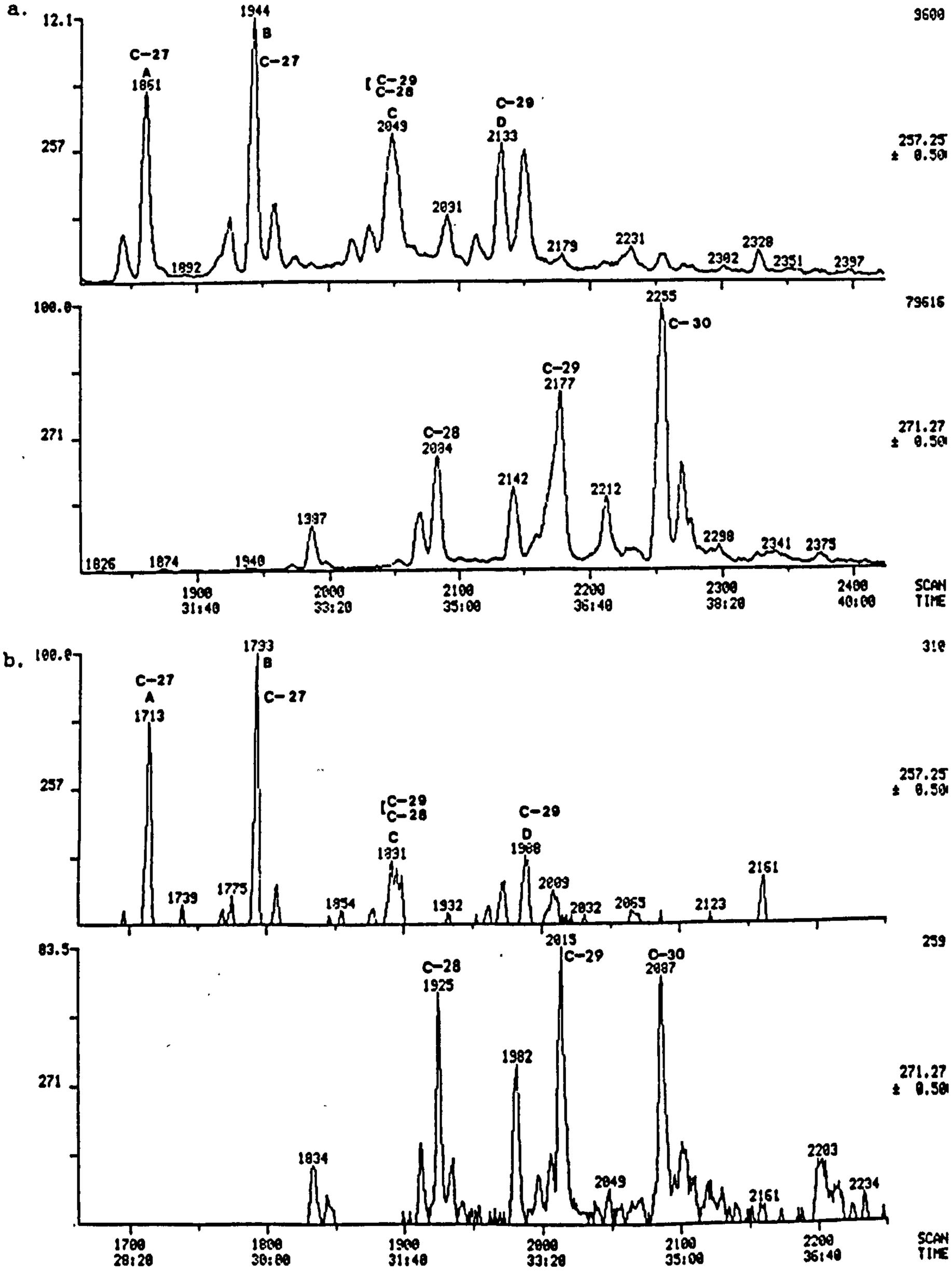


Figure 3.17. (a) Aust Cliff (b) Penarth. Partial mass fragmentograms of m/z 191 and RIC illustrating the distribution of hopanoid components and their homologues.

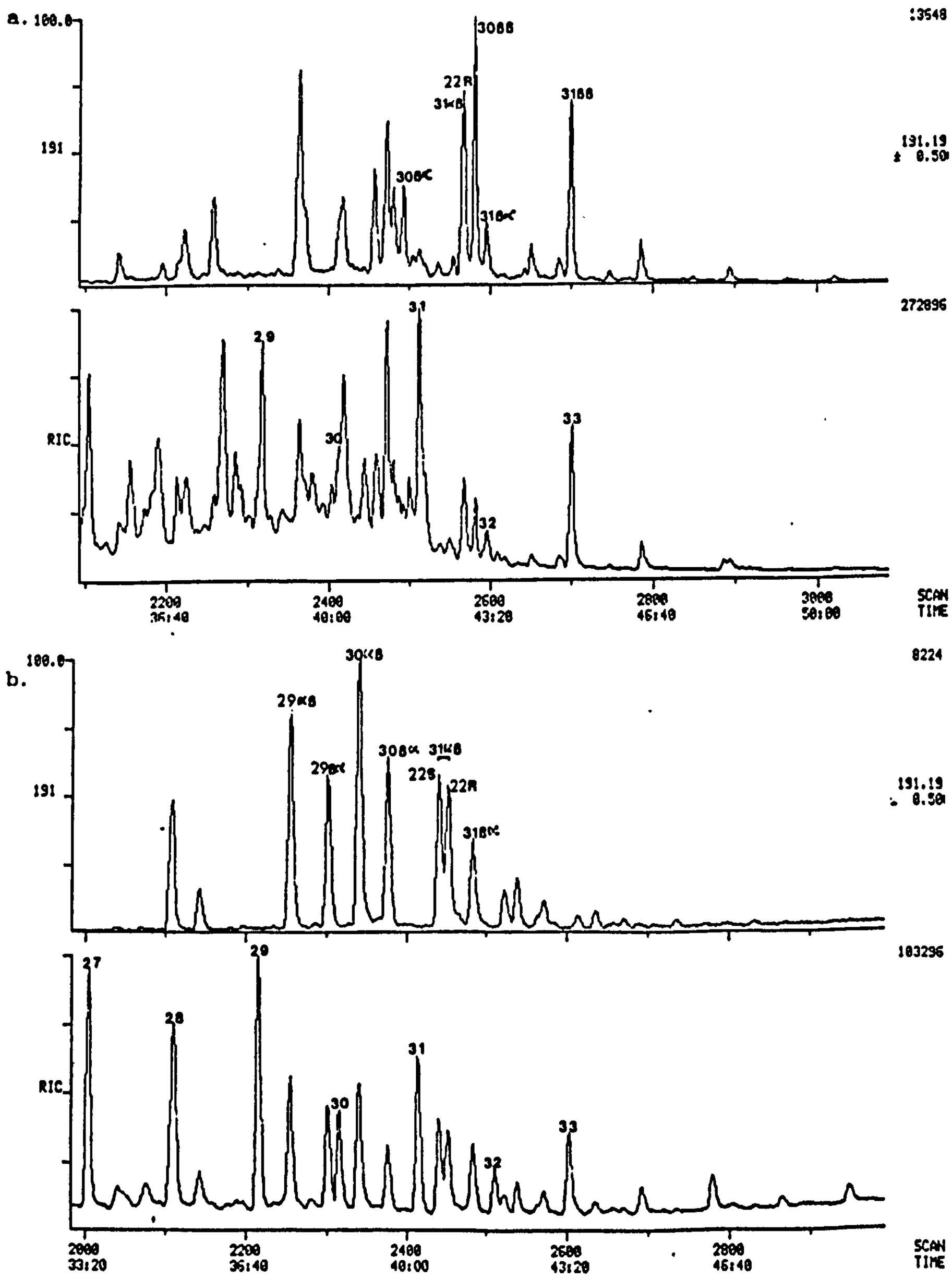


Figure 3.18. (a) Aust Cliff (b) Stowell Park. Partial mass fragmentograms of m/z 217 and m/z 231 illustrating the distribution of steroidal and 4-methylsteroidal components.

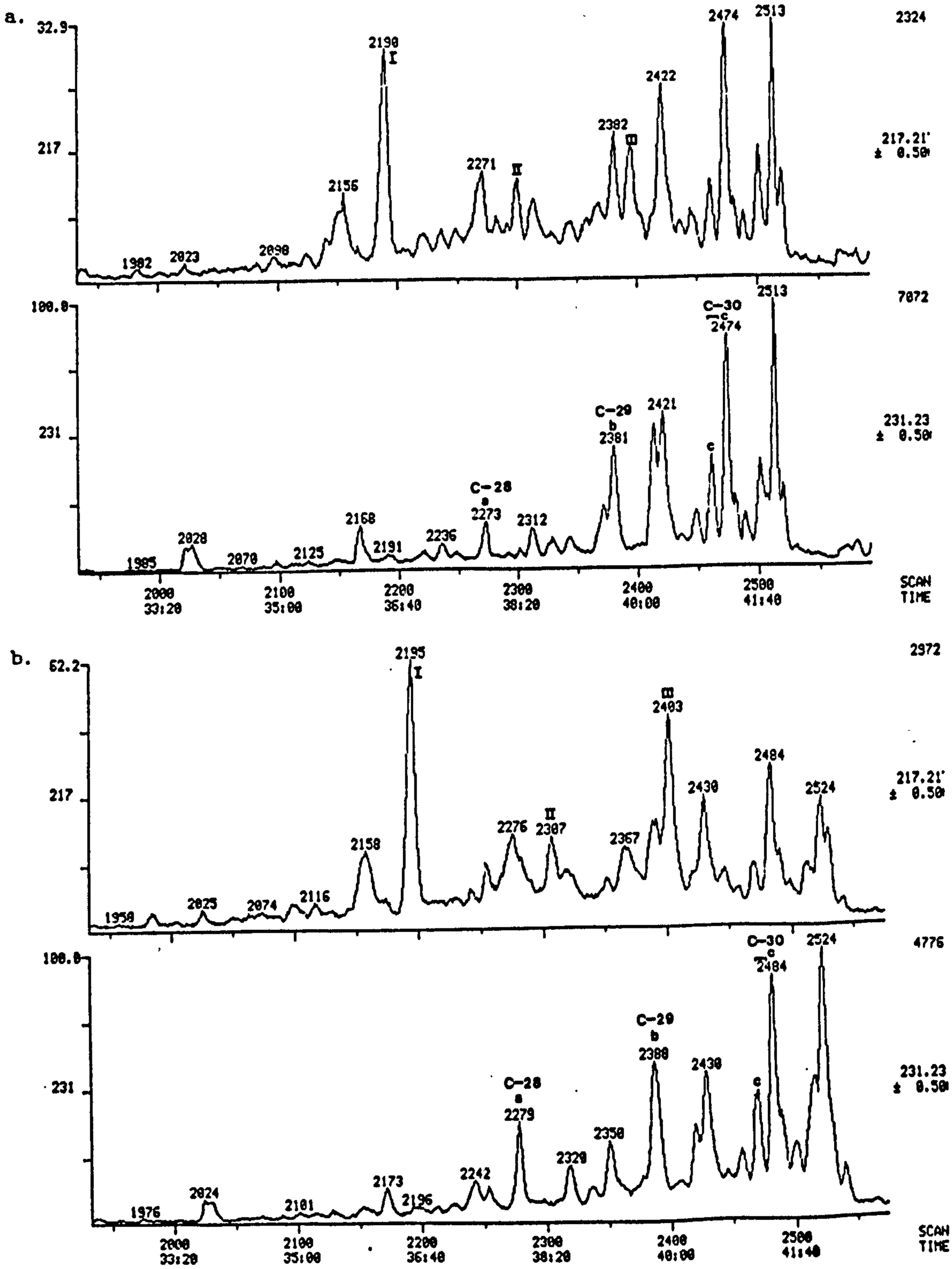


Figure 3.19. Ternary diagram plotting the amount of the C-27, C-28 and C-29 steroidal components from each locality using m/z 217, m/z 372, m/z 386 and m/z 400 mass fragments, in order to illustrate the distribution of steroidal homologues (see also figure 3.14).

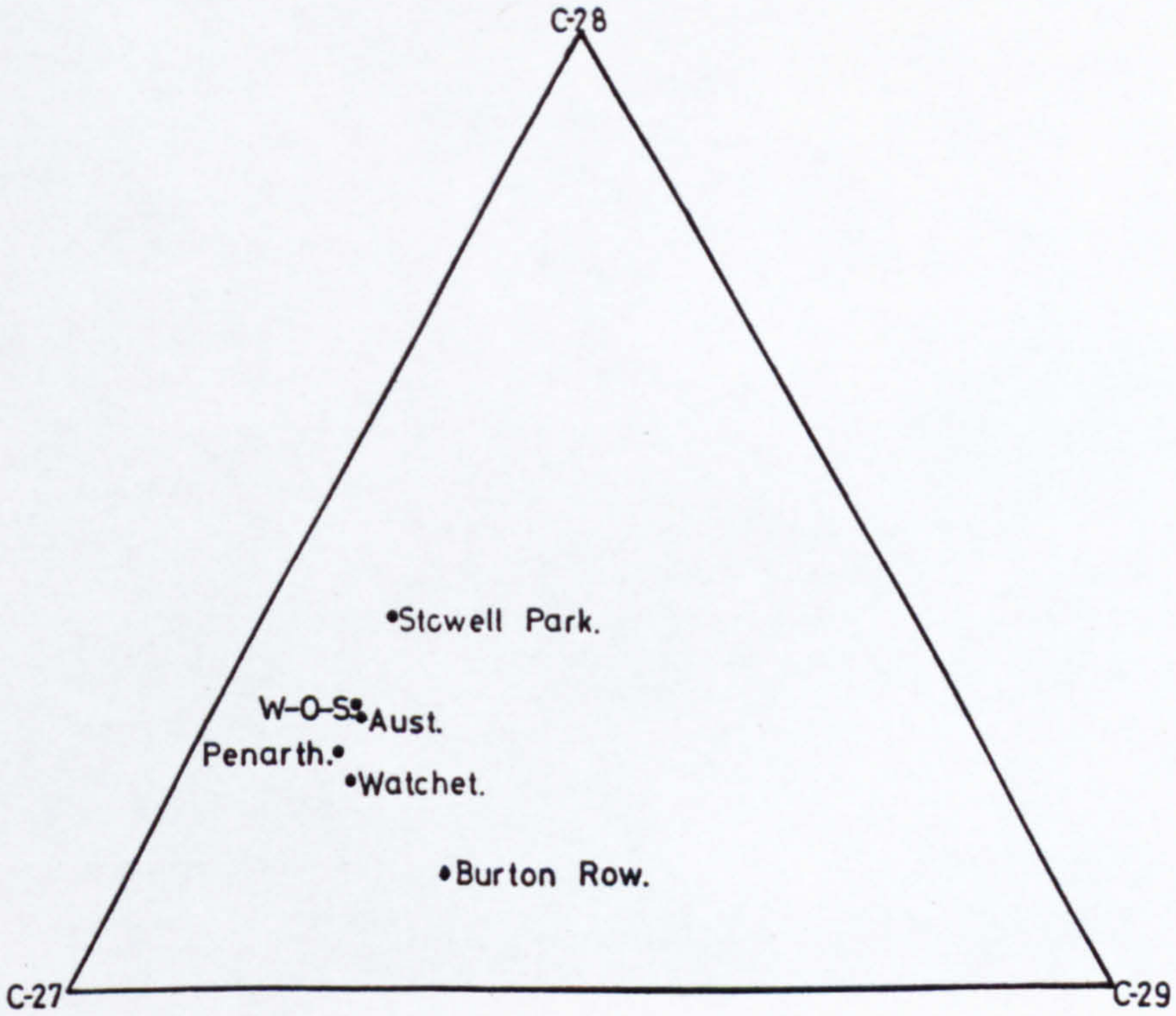


Plate 3.65. Organic rich mudrock.
Structureless organic rich mudrock form Aust 6, (coin 2.5 cm.).

Plate 3.66. Organic rich mudrock (p.p.l.).
Silt grade quartz (Q), organic matter, pyrite (P) and undifferentiated clays from Aust 6.

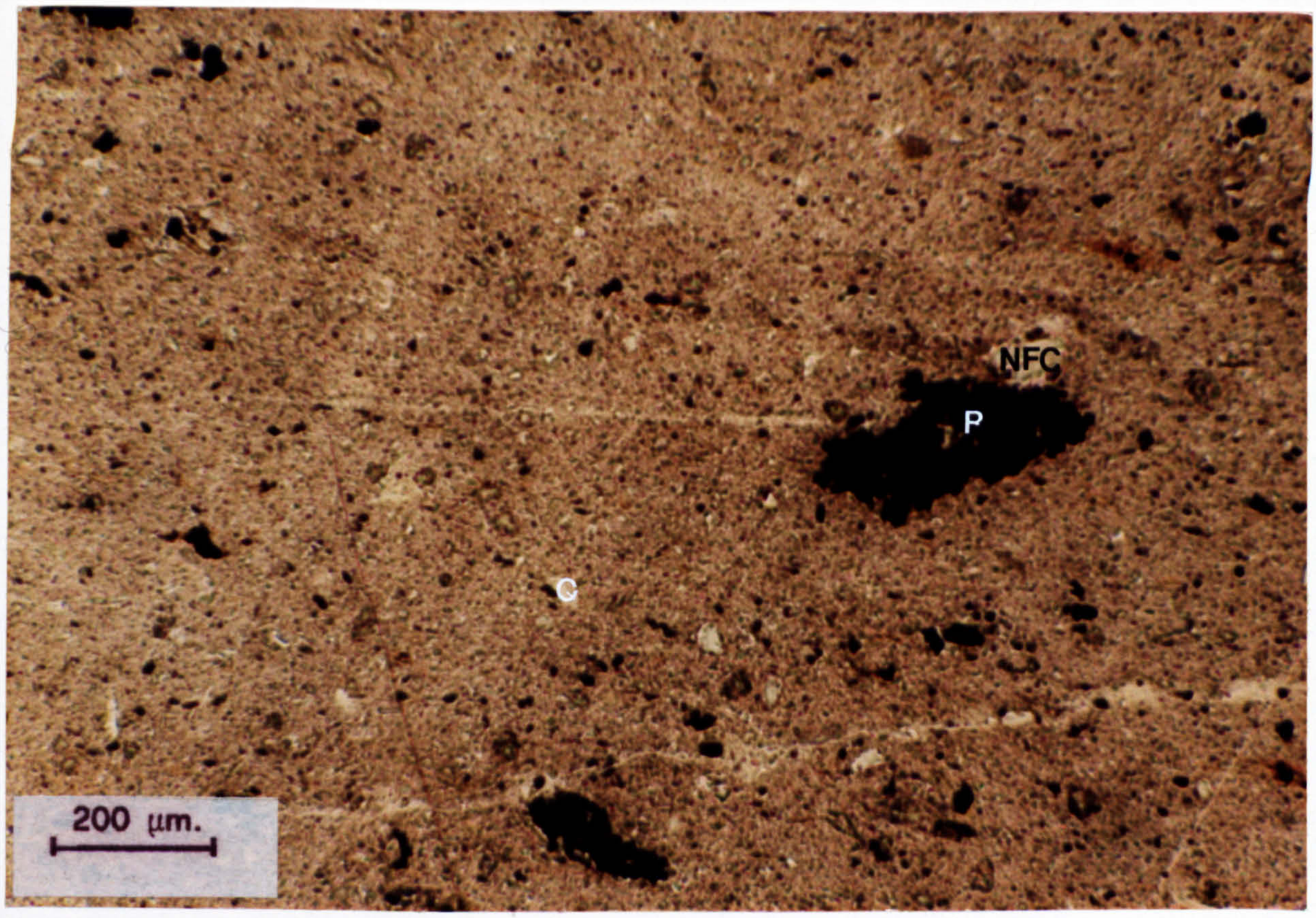


Table 3.1. Selected parameters from the aliphatic hydrocarbon data illustrating provenance and maturity variations between the Worcester Graben and the Bristol Channel Trough.

	Sources of Organic Matter			Maturity of Organic Matter		
	Pr/Ph	Σ 4-Methylsteroids/ Σ Steroids	Σ Hopanoids/ Σ Steroids	CPI ($\underline{n}$-C_{24}-$\underline{n}$-C_{35})	% 22S 17α(H), 21β(H) Homohopane	Σ Diasteranes/ Σ Diasterenes
WORCESTER GRABEN						
Stowell Park	0.6	4.3	0.9	1.9	4.5	0.03
Westbury	0.9	6.9	0.5	2.6	5.0	0.01
Aust	1.2	7.0	0.6	2.7	6.7	0.02
BRISTOL CHANNEL TROUGH						
Penarth	1.9	0.2	16.4	1.5	51.8	3.0
Burton Row	1.7	0.4	5.9	1.1	58.3	1.2
Watchet	2.2	0.6	3.2	1.3	37.3	1.8

Section 3.6b. Facies Interpretation.

The fine grain size and lack of sedimentary structures suggests that these mudstones were deposited in quiet water conditions, at the end of a long sediment transport path. Further - the absence of bioturbation, abundance of preserved organic matter, presence of pyrite and particularly the presence of abundant phytane (table 1) - suggests that deposition occurred in anoxic basins, which periodically developed anoxic bottom water (after Pratt 1984, Potter *et al.* 1980, Didyk *et al.* 1978 and Tissot and Welte 1984).

Most of the preserved organic matter is derived from autochthonous algae, as indicated by the predominance of low numbered n-alkanes (in the range C15-C19), which are derived from the degradation products of tocopherols and chlorophyll molecules (Didyk *et al.* 1978 and Goossens *et al.* 1984). However some of the organic matter has a higher plant ester source as indicated by the presence of C-29 n-alkanes (Eglinton and Hamilton 1963, Simmoneit 1978). The autochthonous nature of the organic matter is confirmed by predominance of C-27 sterane compounds as opposed to the C-28 and C-29 homologues and the presence of abundant 4-methylsteroids. 4-methylsteroids are the degradation products of 4-methylsterols, which are characteristic dinoflagellate marker compounds (Wolff *et al.* 1985, Boon *et al.* 1979, de Leeuw *et al.* 1983 and Robinson *et al.* 1984). The presence of abundant dinoflagellate biomarkers whilst not specific indicators of any particular depositional environment, have only previously been observed in the marine Messel shale (Rubinstein and Albrecht 1975, Wolff *et al.* 1985, which is circumstantial evidence suggesting that these mudstones were deposited in marine conditions (Macquaker *et al.* 1985).

Sulphides are produced by bacterial sulphate reduction of dissolved pore water sulphate in anoxic sediments. The sulphate reducers utilise the sulphate as an electron accceptor to oxidize the organic matter, and in the process produce reducing pore water conditions (Berner 1970, 1978, 1979,

1981, 1982, 1984, Berner and Westrich 1985, Raiswell and Berner 1985 and Postgate 1979). The presence of abundant pyrite also suggests that depositional conditions were marine (as sea water contains considerably more sulphate than freshwater) or if not, at least beneath a water column which contained considerable concentrations of dissolved sulphate (Berner 1981 and 1984).

It is not obvious from where the iron for pyrite formation in the Westbury Formation derived. In modern systems iron usually enters the sediment via iron oxide coats, within clays, as soil sesquioxides and complexed in organic matter (Curtis 1980). However in this context it is not clear which of these sources if indeed any contributed iron to the sediment.

The presence of abundant hopanes indicates considerable bacterial modification of the autochthonous organic matter and possibly an input from cyanobacteria (Ourisson *et al.* 1979 and Brassell *et al.* 1981). Some of this modification was almost certainly due to archaebacterial catabolism, as indicated by the presence of high concentrations of phytane (Holzer *et al.* 1979), and C25 and C30 isoprenoids (Holzer 1979 and Brassell *et al.* 1981). It is worth noting that phytane is also derived from the diagenetic breakdown of ester lipids (Tornabene and Langworthy 1979).

Clearly early diagenetic processes in the mudstones were dominated by the effects of bacterial catabolic processes and in particular by sulphate reducers and archaebacteria e.g. methanogens.

Clues to the deeper diagenetic processes are given by the carbon preference index (CPI) of the C24-C31 n-alkane homologues (Tissot and Welte 1984), the degree of isomerization of hopanes and steranes (Mackenzie *et al.* 1980, Mackenzie *et al.* 1982) and the general ratio of saturated to unsaturated cyclic compounds e.g. the diasterene/diasterane ratios, these key features indicate that none of the samples have reached the oil generation threshold. Consequently it is likely that the well crystallized illite-kaolinite clay

assemblage are detrital components (Hower 1981), whilst the poorly crystalline illite-smectite "mixed-layer" minerals are authigenic (Hower 1981). The presence of these authigenic clay minerals indicates that their component ions were present in the pore waters during burial, which suggests that at least some of the detrital phases (presumably those which were poorly crystalline) were in disequilibrium with their pore waters and that their dissolution supplied the necessary ions for the development of the "mixed-layer" minerals.

Section 3.7a. Fossiliferous mudstones.

Fossiliferous, microlaminated mudstones are common in the Westbury Formation (plate 3.66). They are composed of a silt grade quartz and K feldspar, a clay grade, illite-kaolinite assemblage and locally an illite/smectite poorly crystalline "mixed-layer" phase (figure 3.20). They also contain up to 10% organic matter and significant quantities of pyrite. They differ from the mudstones by containing locally abundant, decalcified shell pavements composed of crushed bivalve debris (plate 3.66). The bivalves are preserved convex-up, disarticulated and normally without any preferred orientation.

The organic matter like that contained within the detrital mudstones is dominated by the presence of odd numbered acyclic n-alkanes (figure 3.11, figure 3.12 and figure 3.13), isoprenoids (figure 3.11, figure 3.12 and figure 3.13), steranes (figure 3.14), diasteranes (figure 3.15), 4-methyldiasterenes (figure 3.16), 4-methysteroidal components (figure 3.18) and hopanoids (figure 3.17).

Plate 3.67. Fossiliferous organic rich mudrock. Predominantly decalcified bivalves (Bv) in an organic rich mudrock, the bivalves are preserved convex-up. Some calcite is still preserved associated with the shelly material.

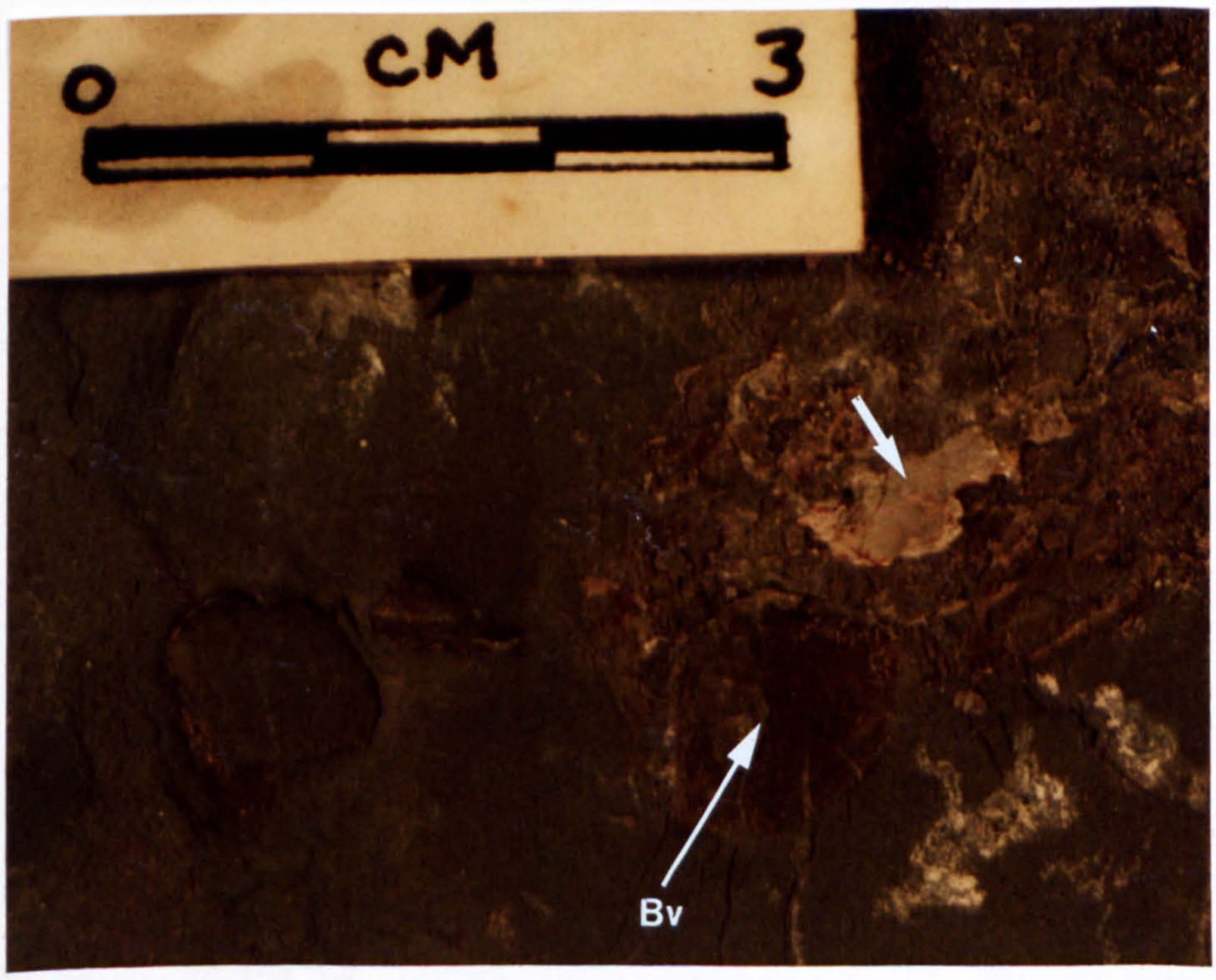
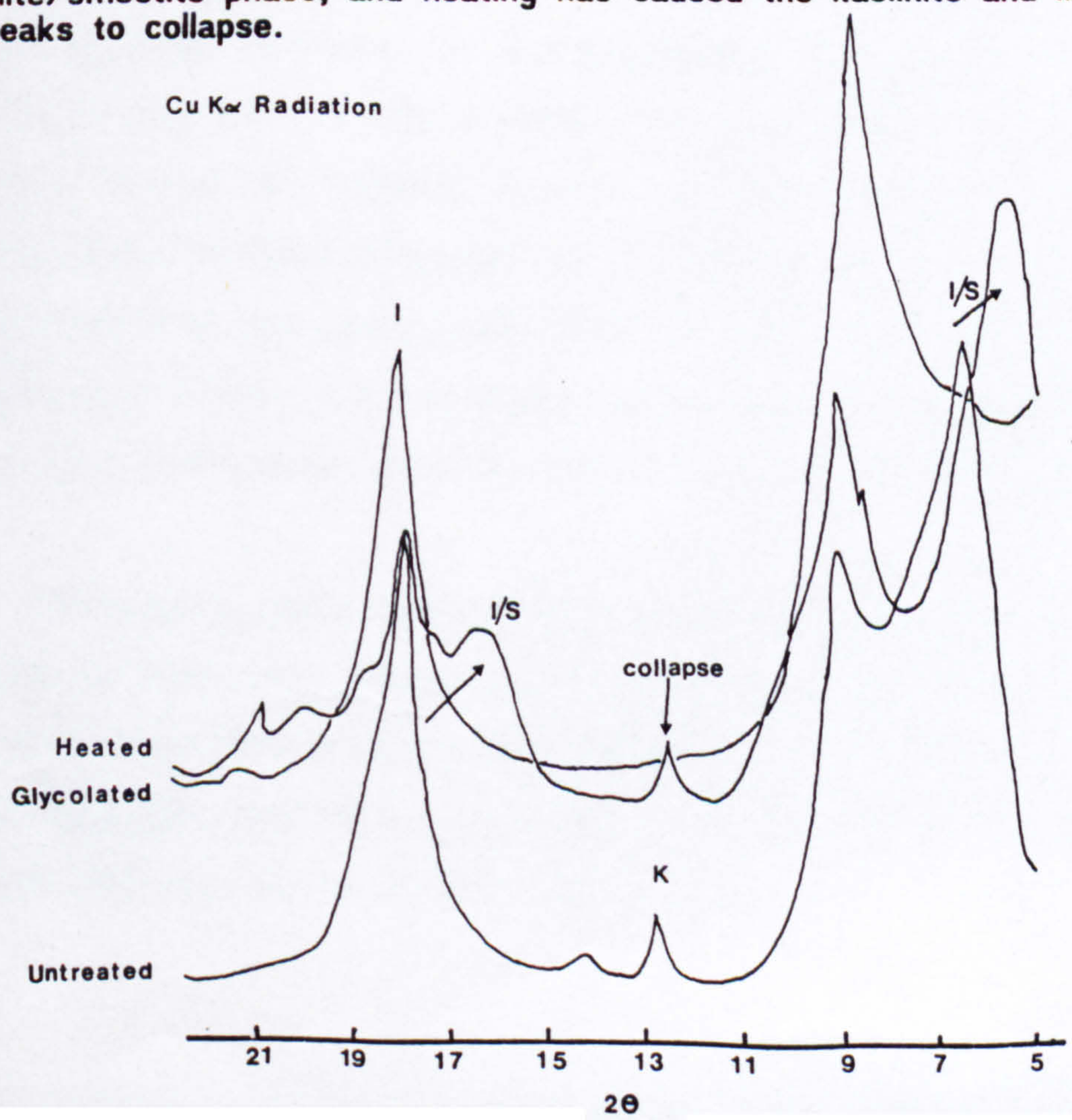


Figure 3.20. X-ray spectra of the untreated, glycolated and heated <2um. fraction, from Upton 6. The dominant clays are illite (I), kaolinite (K) and illite/smectite (I/S) "mixed-layer" phase. Glycolation has caused the expansion of the d-spacing and thus a move to lower two theta values in the illite/smectite phase; and heating has caused the kaolinite and illite/smectite peaks to collapse.



Section 3.7b. Facies Interpretation.

The dominant input into the fossiliferous mudstones was silt grade quartz and an illite-kaolinite detrital clay assemblage. The fine nature of this input suggests that most of the sediment had a long transport path. Occasionally disarticulated, convex-up bivalve shells were also carried into the basin quite often in large numbers. These bivalves are assumed to have a local source as they are unbroken, however the animals from which they were derived were not living *in situ* as the sediment and frequently the bottom water were anoxic as indicated by:- the very high proportion of preserved organic matter, the Pr/Ph ratios, (after Didyk *et al.* 1978 and Tissot and Welte 1984) the preservation of microlaminations (indicating an absence of bioturbation) and the presence of abundant pyrite (indicating reducing and anoxic conditions in the sediment) (Berner 1981). The fact that the shells have been transported is further indicated by the preponderance of bivalves preserved in their current stable position - convex-up (Ivimey-Cook 1962) and the unequal distribution of the valves (Bazley 1968). It is worth noting that these transporting mechanisms however did not aerate the sediment as there is no evidence of bioturbation and the organic matter is not significantly oxidized (as indicated by high total organic carbon (T.O.C.) concentrations in the fossiliferous units which are similar to that in the non-fossiliferous mudstones, Jones 1981); neither did they carry in coarse clastic detritus or produce any current bedforms. Overall this suggests that the transport processes were local, relatively short duration phenomena and as the shell pavements are rare, probably occurred only occasionally. With this in mind and the fact that there is evidence of storms in other closely related (both temporally and spatially) facies, local storm surge currents are the proposed transporting mechanism.

The organic matter input into the basin during deposition of the fossiliferous muds was more or less indistinguishable from that during the deposition of the detrital muds, being dominated by an autochthonous algal and dinoflagellate input which was subsequently modified by bacteria (and has been characterized in detail in section 3.6b).

The diagenesis of these fossiliferous black muds, is considered to have been similar to that occurring in the detrital muds; With the early formation of pyrite and the modification of the organic matter being initially bacterially mediated, (in particular by sulphate reducers) with the further modification of the organic matter and the formation of an illite/smectite "mixed-layer" phase occurring during later burial. The main difference in the diagenetic process between the two facies, is the dissolution of metastable aragonitic bivalve debris; which presumably resulted from the development of acidic pore waters either associated with:-

1) Bacterial catabolism (e.g. sulphate reduction) with the formation of hydrogen sulphide in iron limiting environments (Curtis 1980).
2) Sulphide oxidation in interface environments.
3) The release of humic acids or organic acids during burial (Carothers and Kharaka 1978).
4) Methanogenic decarboxylation.
5) Thermal decarboxylation during burial (Curtis 1980).
6) Surficial weathering (Berthelin 1983).

Any of these processes may have caused shell dissolution, although the deeper processes are more likely as the shells are preserved as compacted moulds.

The illite-kaolinite, assemblage is well crystalline which suggests that it has a high temperature origin. As the organic matter has clearly not generated oil and thus has not exceeded temperatures above 60°C (as indicated by the presence of unsaturated alkenes, the hopane isomerization ratios (Mackenzie *et al.* 1982) and the carbon preference index (Tissot and Welte 1984) these clays probably have a detrital origin. In contrast the poorly crystalline illite/smectite phase probably has an authigenic origin, forming during burial where there is dissolved silica, aluminum and potassium in the pore waters, and in conditions where there is not enough potassium to form K feldspar (Hower 1981), which in this context was probably associated with the generation of acidic pore waters.

CHAPTER 4. GENERAL FACIES RELATIONSHIPS.

Section 4.1. Vertical and lateral relationships between facies.

The six Westbury Formation facies are vertically separated from one and another by erosional and diagenetic "surfaces". These "surfaces" are then either obscured or enhanced by subsequent processes e.g. cementation, neomorphism or bioturbation.

Erosional surfaces are present between the two major facies, namely the detrital mudstones and fossiliferous mudstones and also on the base of the arenaceous units between them and the detrital mudstones. They also occur between some of the microfacies, e.g. between the arenaceous sandstones and the lithoclastic packstones.

Gradational contacts only exist in a true sense i.e. as fining upward cycles, between the packstones and detrital wackestones. True fining upward relationships are not present between the arenaceous units and the detrital mudstones, as they are separated by a significant depositional hiatus; a fact indicated by the abundant feeding trails on the top surface of the former.

Many of the nodular wackestones are in abrupt contact with the surrounding detrital mudstones. The surfaces between these facies do not appear to relate to "sedimentological events", instead they are interpreted as having a diagenetic origin, being formed as a consequence of nodule growth within the sediment as a result of anaerobic bacterial catabolism.

Laterally most of the facies, with the exception of the diagenetic wackestones, interdigitate with one and another, both on the small scale (a few centimetres) and on a larger scale (10's metres). Thus detrital mudstones interdigitate with fossiliferous detrital mudstones, packstones,

arenaceous sandstones, calcarenaceous sandstones and detrital wackestones and vice-versa. A fact which presumably reflects an intermittent and variable supply of coarse detrital debris in otherwise mud dominated sedimentary regimes.

In conclusion most Westbury Formation facies are vertically separated from one and another by erosion events, these events truncate the different facies, producing coarsening upward cycles of units with different grain size or grain components. True fining upward cycles are only observed where lithoclastic packstones and calcarenaceous sandstones grade upwards into detrital wackestones. Fining upward cycles do not exist in the same manner between the calcareous sandstone units and the detrital mudstones because there appears to be considerable time separation between the deposition of the sands and muds. Abrupt non-depositional, diagenetic relationships exist between the wackestones and the detrital mudstones. Finally most of the facies laterally grade into one and another, as a consequence of the intermittent supply of coarse detrital debris in a mud dominated sedimentary system.

Section 4.2. Regional facies variation.

The Westbury Formation does not significantly vary its thickness at any of the studied localities, from a maximum of 7.5 metres at Burton Row, to a minimum of 3 metres at Three Arches Bridge, with most localities being approximately 4.5 metres thick.

Within the Westbury Formation individual units are generally not correlatable with any certainty between adjacent localities, with the possible exception of those in South Wales and certainly not between the two tectonic basins. This poor lateral correlation is caused by the major carbonate and clastic units tending to thin laterally on a kilometre scale (e.g. bed 2 at Aust which is only present in the northern part of the section).

Interestingly the six facies are not developed equally at all the sample sites; for instance diagenetic wackestones are only present within the Bristol Channel Trough and are not observed in the Worcester Graben. In addition the carbonate units in the Worcester Graben appear to have suffered less fabric destructive cone-in-cone formation but more intense recrystallization of the biogenic debris and micrite. A significant authigenic clay assemblage has only been observed at Upton where it comprises a randomly interlayered "mixed-layer" illite/smectite phase.

Across the study area the grain size variations are minimal, with the dominant clastic input at all localities being a detrital silt grade quartz and K feldspar assemblage, coupled with a clay grade, detrital illite-kaolinite assemblage (see appendix 3). Occasionally however mud sedimentation was disrupted by a coarser clastic input which is dominated by biogenic material (mainly bivalves) and fine/medium sand grade quartz and K-feldspar; which locally at Penarth increases to medium/coarse sand. Phosphatic vertebrate derived debris may also be a significant component of some of these units.

The provenance of the organic matter biomarkers was not found to vary significantly from place to place, being dominated by short chain n-alkanes, with a less important, longer chain n-alkane component. However some differences were observed, notably an increase in the amount of phytane, coupled with a higher carbon preference index, and an increase in the relative proportion of 4-methylsteroids in samples from the Worcester Graben compared with those from the Bristol Channel Trough. Conversely the Bristol Channel Trough samples showed an increase in the relative amounts of hopanoids. The maturation indices revealed by the organic matter indicated that the grabens had a broadly similar thermal history. Although the samples from the Bristol Channel Trough have higher diasterane/diasterene ratios, only 4-methylsteranes and the higher temperature 17 (H) and 21 (H)-hopanes rather than 17 (H) and 21 (H)-hopanes, whilst the lower temperature isomers and 4 - and 4-methylsterenes are present in the Worcester Graben (Macquaker *et al.* 1985).

Section 4.3. Regional facies interpretation.

Detrital sapropelic mudstones are the dominant facies in the Westbury Formation, indicating that the main sediment input was detrital clay, silt and organic matter. These facies were deposited in low energy basins where there was high surface organic productivity and possibly bottom water anoxia. The prevailing anoxic conditions restricted benthic macro-fauna colonization of the sediment, consequently microlamination is preserved.

Rare, coarser clastic units are interbedded with the muds. These intermittent arenaceous units disrupt the background mud sedimentation, and were deposited in infrequent, probably short duration higher energy conditions. These units contain numerous sedimentary bedforms e.g. oscillation ripples, spill over ripples, gutter casts, conglomeratic rip-up clasts, graded rhythmites, fining upward sequences, internal scour surfaces, basal scour surfaces with tool marks, convex-up, end-on and disarticulated shelly debris and were oxygenated as indicated by the bioturbation. Using modern analogous sediment sequences described by Reineck and Singh (1980), and fossilized sediments described by Aigner (1982), Reif (1982) and Kreisa and Bambach (1982) it is likely that the coarse interbedded units were deposited during rare storm surge events. These storms supplied autochthonous clastic debris and aerated the sediment and were rare events when viewed against the background low energy anoxic deposition. Using Aigner's (1982) criteria, the storm sequences preserved in the Westbury Formation are proximal facies, as they are fairly thick bedded, often contain rip-up clasts and tend to be superimposed upon one another. The latter being indicated by the relative scarcity of fining upward cycles and the dominance of internal erosion surfaces, which implies that the storms remobilized part of the sediment deposited by an earlier events. The sediments were often sufficiently oxygenated by the storms to allow brief periods of opportunist macrofaunal colonization.

Modern storm facies are not traceable over large regions (Specht and Brenner 1979, Aigner 1982, Kreisa 1981) because deposition only occurs in local areas. Unsurprisingly therefore the Westbury Formation storm beds are not regionally correlatable.

Sedimentation across the study area was remarkably uniform, particularly during fair weather conditions, when it was dominated by fine mud and clays comprising quartz, K-feldspar, illite and kaolinite. During storm conditions the coarser clastic siliceous debris probably had a fairly local provenance, either being derived from the nearby land masses or from reworked earlier sediments. The abundance of K-feldspar is particularly interesting as it was probably derived from the Pennant Sandstone or from earlier volcanic sediments on the Mendips or in South Wales. This provenance maybe analogous to examples reviewed by Kastner (1971) where she found that K-feldspar in marine sequences had a metamorphic or igneous origin. Mayall (1979) assumed that the illite/chlorite detrital assemblage in the Westbury Formation had a similar source to the K-feldspar.

The shelly material is assumed to have also been reworked by storms from oxic parts of the basin and transported presumably offshore into deeper anoxic regions. Clearly with the exception of some of the storm units, most of the animals were not living *in-situ*, (it is worth noting however, that some bivalves will respire using sulphate as an electron acceptor or by living symbiotically with methanogens (Bosence pers. comm. 1986, Suess pers. comm. 1985)). The shells often preserve fine ornamentation (despite being decalcified) and thus were probably not transported far, which is in accordance with observations by Kresia (1981) on modern sediments, who noted that hurricanes did not cause mass shell transport over long distances, except where rip currents were significant and where debris is moved offshore from the beach face above fair weather wave base.

The organic matter provenance varies slightly between the samples in the Bristol Channel Trough and the Worcester Graben. Both sample suites are characterized by having a dominant marine algal and bacterial input that has been subsequently bacterially modified, as indicated by the dominance of low numbered n-alkanes, and the presence of steranes and hopanes. However the proportion of individual components may vary significantly. For instance:-

i) The pristane/phytane ratios which indicate both maturity and provenance variations for the organic matter between the two grabens. The lower ratios observed in the Worcester Graben may reflect less lipid breakdown of chlorophyll degradation products (Tissot and Welte 1984) or an increased phytane contribution from archaebacteria (Brassell *et al.* 1981). Whilst the higher ratios in the Bristol Channel Trough may reflect either slightly increased lipid oxidation in the water column (Tissot and Welte 1984) or increased pristane input from zooplankton (Blumer *et al.* 1963). (It is worth noting that increased pristane phytane ratios are also observed with increasing maturity (after Tissot and Welte 1984)).

ii) Increased amounts of 4-methylsteroids are preserved in the Worcester Graben (table 4.1) which indicates that dinoflagellates were the major contributors to the preserved organic matter in this basin (after Wolff *et al.* 1985).

iii) Interestingly the organic matter from the Bristol Channel Trough has an increased hopane/sterane ratio (table 4.1), which implies that its autochthonous organic matter was subject to greater bacterial modification Macquaker *et al.* (1985).

Overall the biomarkers suggest that the organic matter in the Bristol Channel Trough spent slightly longer in oxic conditions (possibly in the water column) and that it was more modified by bacteria. Whilst the samples from

the Worcester Graben had an increased organic input from dinoflagellates and local conditions were slightly more reducing. The interesting empirical observation that cone-in-cone carbonates are more common in the Bristol Channel Trough than the Worcester Graben and that metastable carbonates have undergone increased recrystallization in the latter, may relate to the presence in the Worcester Graben of increased concentrations of dissolved sulphides. Increased sulphide concentrations may cause the early inversion of aragonite to low Mg(II) calcite (Bathurst 1975). Assuming this process to have occurred in the Worcester Graben, it would pre-empt later solution and reprecipitation of aragonite which might otherwise form cone-in-cone calcite and it would form abundant neomorphic textures. Conversely in the Bristol Channel Trough where conditions were less reducing, aragonite was preserved long enough to be mobilized during burial to form cone-in-cone structures.

Diagenetically the thermal histories of the grabens are very similar, with neither having generated oil. Mackenzie *et al.* (1980) and Mackenzie *et al.* (1982) showed experimentally using organic matter buried in the Paris Basin that hopane and sterane isomerization is temperature controlled. Using the constraints erected by these workers it is clear from the presence of i17β(H), 21α(H)- and 17α(H) and 21β(H)-hopanes in the Worcester Graben as opposed to the presence of 22S 17β(H), 21β(H)-homohopane (table 4.1) in the Bristol Channel Trough that the samples from the latter are more mature than those from the former. This is backed up by the decreased carbon preference index (implications reviewed by Tissot and Welte 1984), the increased diasterane/diasterene ratios and the presence of 4α-methylsteranes in the samples from the Bristol Channel Trough, whilst the Worcester Graben samples contain 4α- and 4β-methylsteranes (after Wolff *et al.* 1985) which indicates that they are less mature. Authigenic clays are only present at one locality, namely Upton and include a poorly crystalline illite/smectite "mixed-layer" assemblage.

CHAPTER 5 GENERAL INTERPRETATION.

Section 5.1. Environment of deposition.

The Westbury Formation in south-west Britain was almost certainly deposited in marine, predominantly stratified anoxic basins, which had anoxic hypolimnia, as indicated by the preservation of abundant organic matter (see below) and authigenic pyrite; occasionally however the bottom waters were oxygenated, as indicated by the preservation of rare bioturbated units in otherwise unbioturbated sediments. This intermittent oxygenation of the sediment created sub-oxic pore waters, as indicated by the presence of glauconite which only forms in interface redox environments (Curtis pers. comm.).

The presence of a shelly macro-fauna throughout the sequence does not aid detailed facies interpretation as it is not preserved *in situ*. Despite this however it is possible to make gross generalizations about depositional conditions, as by and large the fauna is unbroken and has not been transported far. Thus the presence of echinoderms, brachiopods and sharks suggests that normal marine conditions existed either above the hypolimnia or in the marginal basin areas, since most modern examples of these groups are stenohaline (Schaffer 1972 and Duffin 1978). Reynolds (1947) and Duffin (1978) suggested that some of the phosphatic material had an amphibian origin, hence depositional conditions in their view were brackish. This material however has been re-examined by Savage and Large (1966), whom proposed instead that it was derived from palaeniscid fish, consequently it can not be considered to be a reliable brackish water indicator. Similarily the presence of *Ceratodus sp.* has been used as an indicator of brackish water deposition (Reynolds 1947). However *Ceratodus sp.* has been found associated with ammonites in Alpine Triassic sediments (Martin pers. comm. 1981), thus it too is not considered a reliable depositional marker.

The preserved organic matter in the Westbury Formation also indicates marine deposition, as it is dominated by biomarkers from autochthonous marine algae, dinoflagellates, cyanobacteria and bacteria, rather than being dominated by higher plant derivatives.

During deposition of the Westbury Formation the sediment/water interface was almost certainly, albeit only for brief periods, in the photic zone, as indicated by the presence of:- algal lamination, coated grains and micrite envelopes, assuming of course that the latter was formed by endolithic algae, rather than by fungi. There is no evidence of emersion during deposition, and it is likely that as storm waves only intermittently reworked the sediment, that water depths were between storm and fair weather wave base. Despite this however as deposition was occurring in restricted basins with possibly limited fetch, water depths may not have been great.

In conclusion therefore deposition probably occurred in predominantly anoxic basins, in the photic zone, above storm, but below fair weather wave base and in water depths between 10 and 30 metres.

Section 5.2. Controls of sedimentation style.

i) Anoxic sedimentation.

Anoxic sediments form wherever oxygen demand exceeds oxygen supply. This occurs wherever aerobic respiratory process use up oxygen faster than it is replaced by flushing or diffusion from the overlying water column. Fine sediments which are buried in low energy conditions, with large amounts of organic matter are particularly susceptible to becoming anoxic, as flushing is limited and the relative amounts of aerobic respiration are high. The converse is true for coarser sediments, which have increased porosity and thus are better flushed by oxygen rich water. Hence grain size, organic matter input, deposition rates and ambient energy levels are the main factors controlling sediment anoxia (Curtis 1980).

Demaison and Moore (1980) recognise four main modern environments where anoxic muds are deposited. These are summarized and discussed below, and particular attention is paid to the depositional conditions under which the Westbury Formation muds may have been deposited:-

(a) Large anoxic lakes.

Temperature stratification in some lakes causes the development of a thermocline that inhibits complete overturning of the lake water. Waters beneath the thermocline are then susceptible to becoming anoxic, if sufficient organic matter is entering the system to cause abundant aerobic respiration and depletion of the oxygen in the stagnant water.

(b) Anoxic silled basins.

Silled basins may become anoxic if they are cut off from oceanic circulation patterns and where fresh water input exceeds evaporation. The input of freshwater causes positive water flow movements to develop in the water column, which leads to salinity stratification (a halocline) and prevents efficient bottom water turn over. Aerobic organisms living beneath the halocline quickly deplete the available oxygen and cause bottom water anoxia. Classic modern examples of anoxic silled basins include the Baltic and Black Sea. It is worth noting that the Mediterranean despite being a silled basin does not become anoxic, due to evaporation exceeding freshwater input, and hence the development of a negative water flow which carries oxygen rich water into the deeper parts of the basin.

(c) Anoxic layers caused by oceanic upwelling.

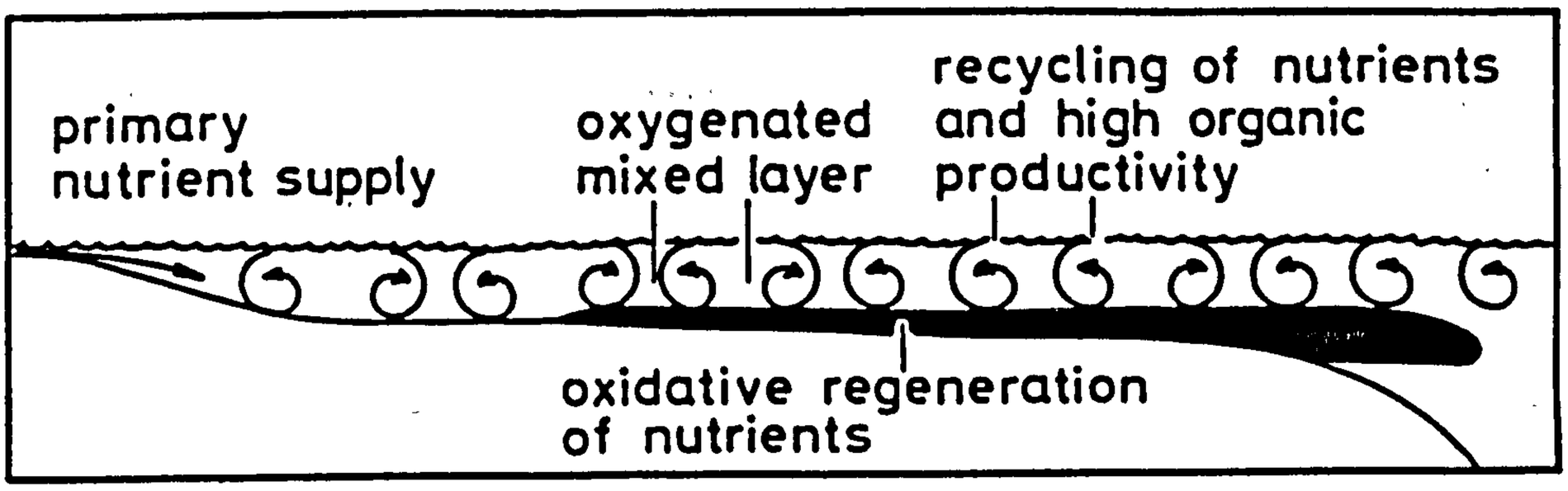
Oceanic upwelling is caused by bottom, cold currents, often nutrient rich striking the shelf edge and being forced into the surface water layers. This recycles otherwise limiting nutrients (phosphate and nitrates) to phytoplankton and causes a marked increase in organic productivity. Coupled with this increase of surface productivity more organic detritus is supplied to the sediment, which increases the relative number of aerobic organisms living there. Consequently the sediment may become anoxic if the oxygen supply cannot meet the increased demand (although it often does). Modern examples of upwelling causing anoxia occur on the Peruvian Shelf.

(d) Open ocean anoxia.

Open ocean anoxia is caused by water masses at intermediate depth, being depleted of oxygen by aerobic biological activity and being a long way from their oxygen source. The main source of oxygen in the oceanic water column is the cold polar regions, where there is a negative water flow from the oxygenated surface waters to the sea bed. In regions well away from the poles and depleted by aerobic respiration, open ocean anoxia develops.

It is clear that the only model of anoxia remotely analogous to the depositional conditions present in the Westbury Formation is the silled basin type. Anoxic lakes are rejected because deposition during the Westbury Formation occurred in marine conditions (on the basis of faunal and geochemical evidence). The open ocean anoxia model is also not suitable, because the Westbury Formation in south west Britain was deposited in a shelf sea on a blind arm of Tethys (Ziegler 1982), whilst anoxia as a consequence of upwelling is rejected both for the latter reason, and because Britain was nowhere near a shelf edge at this time (Parish and Curtis 1982). Despite rejecting the alternative models the silled basin hypothesis does not adequately explain anoxia in the Westbury Formation as there is no evidence of large scale freshwater input into this basin - indeed Whiteside (pers. comm. 1984) suggested that local terrestrial conditions at this time were semi-arid. Thus the Baltic and Black Sea, which are often cited as being modern Westbury Formation analogues (e.g. by Hallam and Sharraway 1982) are not particularly useful models. Indeed if one assumes Whiteside's speculations to be correct then the water column in this part of Tethys may have developed a negative water flow. Schlanger and Jenkyns (1976) and Jenkyns (1980) however provide a suitable modification to the silled basin model. They suggested that high surface productivity fueled by nutrient runoff from the land, might cause bottom water anoxia, where there was a lack of oceanic circulation, with only wave activity reworking the top part of the water column (figure 5.1). Such a modification provides a plausible explanation for Westbury Formation anoxia, and provides the opportunity for storm waves to temporarily cause the complete oxygenation of the water column and the sediment.

Figure 5.1. The development of anoxic bottom waters as a result of high surface productivity. High surface productivity is maintained by nutrient input from terrestrial runoff and storm recycling of anoxic bottom water (after Jenkyns 1980).



(ii) Limestone shale cyclicity.

The origin of limestone/shale cycles and rhythmic sedimentation in general has been reviewed by Einsele and Seilacher (1982), Schwarzacher (1975, 1982) and in particular by Einsele (1982). In the Westbury Formation sedimentary cyclicity is linked to the intermittent availability of oxygen and input of coarse clastic material into predominantly anoxic muddy sediments, which in this case is assumed to be caused by rare storm events in otherwise quiet water conditions. Despite this obvious primary sedimentary control however, diagenesis has played a significant role as cementation and dissolution have either emphasised or disguised the primary sedimentary fabrics. A fact indicated by the bivalve decalcification in the detrital fossiliferous mudstones, and microsparry calcite precipitation in the diagenetic wackestones. Thus in the Westbury Formation, the observed limestone/shale cyclicity is a product of both sedimentary and diagenetic processes.

The predominance of anoxic shale facies in the Westbury Formation implies that most deposition was occurring during low energy conditions. Storm units comprise less than 10% of any section (even after compaction) and therefore would have been extremely rare phenomena on a geological time scale. It is worth

noting that the storm bedded units contain stacked events separated by erosion surfaces, implying that more than one storm reworked the sediment during the periods of high energy activity.

Marsaglia and Klein (1983) and Parrish and Curtis (1982) reconstructed global palaeoclimatological maps; they noted that Tethys in the Upper Triassic was in the hurricane belt. Thus the shelf sea, and associated archipelago at the north-western end of Tethys, that covered southern Britain at this time may have been particularly susceptible to intense summer storms, rather than mid-latitude winter storms, particularly if the hurricane belt was wider at this time, as postulated by Duke (1985). Thus storm sedimentation in the Westbury Formation is considered to be correlated with intermittent hurricane activity (figure 5.2 and figure 5.3) (which aggrees with Aigner's (1982) interpretation of storm sedimentation in the German Muschelkalk).

Figure 5.2. Hypothesized summer weather patterns and the position of the hurricane belt (bold arrows), upwelling zones and regions of "atmospheric highs" (H) (Marsaglia & Klein 1983, Parrish & Curtis 1982).

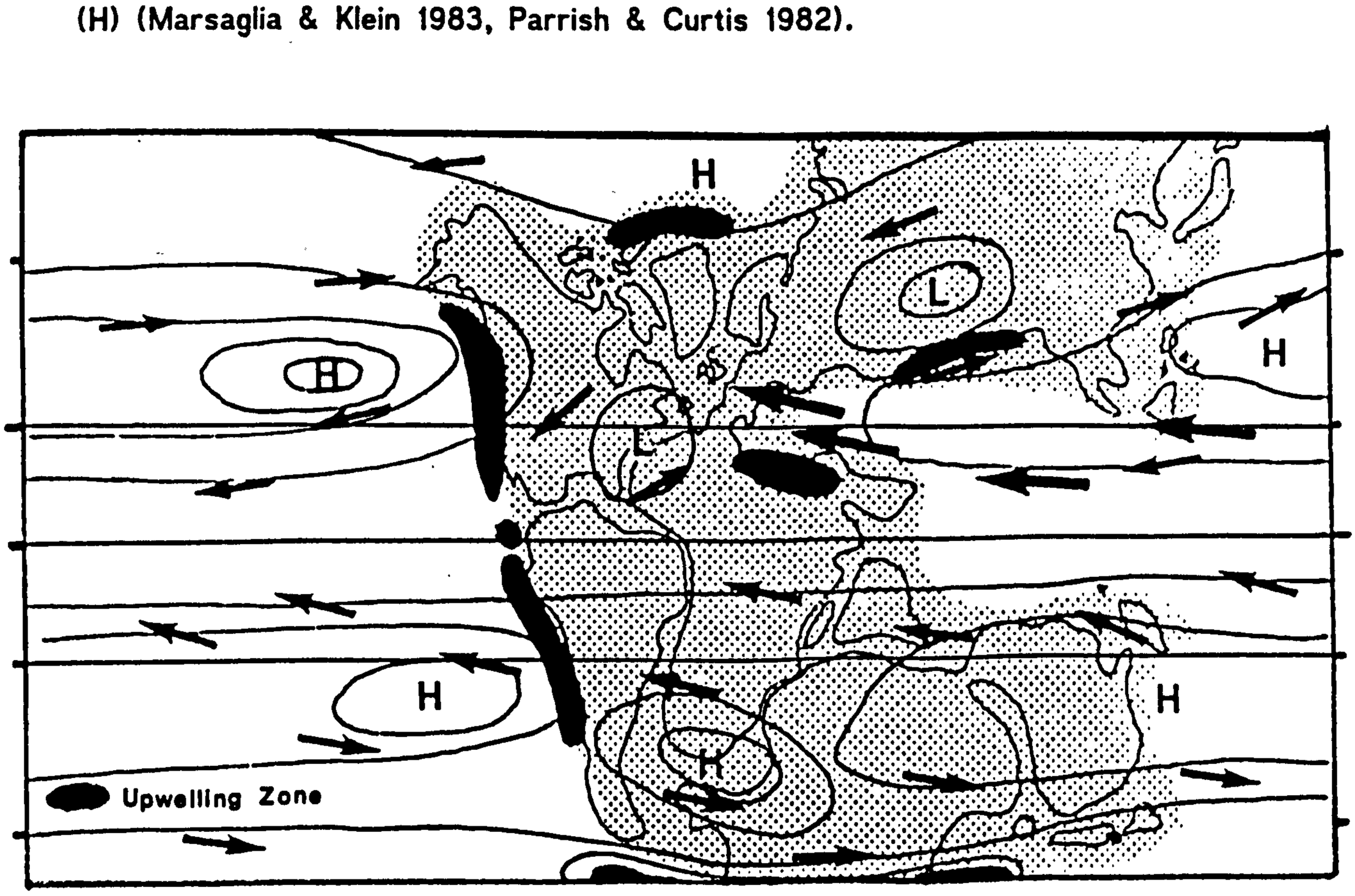
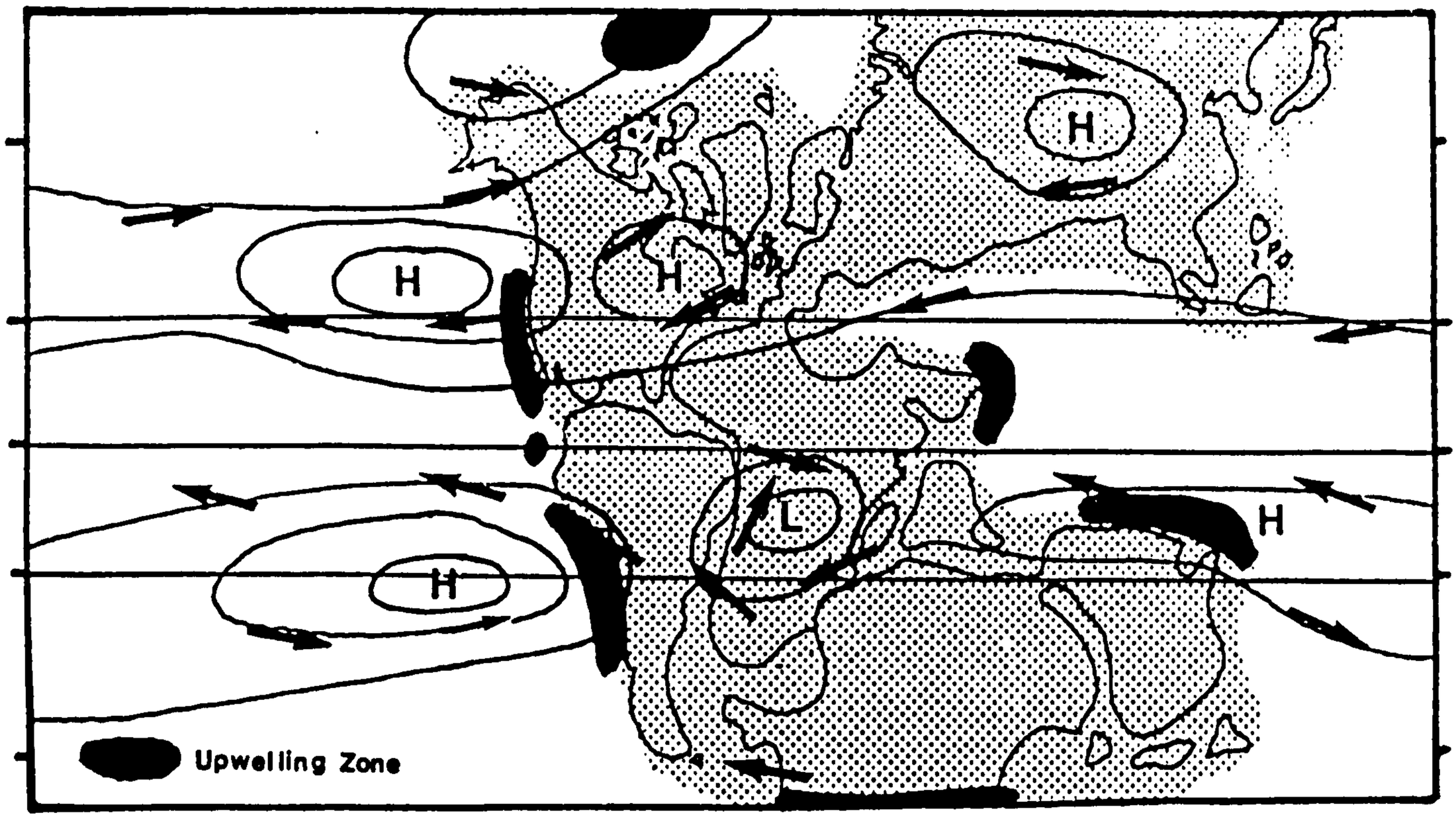


Figure 5.3. Hypothesized winter weather patterns and the position of the upwelling zones and "atmospheric highs" (H) (Marsaglia & Klein 1983, Parrish & Curtis 1982).



Unfortunately it is not sufficient to invoke just intermittent storm activity as the sole cause of limestone/shale cyclicity in the Westbury Formation. This is due to major storm events on a geological time scale occuring frequently and them being rare and restricted to certain horizons in the Westbury Formation. Thus clearly there were significant periods of deposition when storms did not occur, implying that storm activity was restricted to certain time intervals. A number of possible causes may account for this including:-

i) Long term cyclic sea level changes.

ii) Long term cyclic weather changes.

Either one of which might account for the long term cyclicity of fair weather periods interspursed with storms over the duration of deposition of the Westbury Formation and are discussed below.

Sea level changes are controlled by eustatic changes in base level (Hallam 1960, 1961, 1964 and 1969, Duff *et al.* 1967), fluctuations in ocean ridge activity and changes in the amount of water locked up in the ice caps (Imbrie and Imbrie 1979). Previous workers on the Westbury Formation (e.g. Hamilton 1977, Mayall 1979 and Jones 1981) have tended to prefer the eustatic model for controlling sedimentary cyclicity. Primarily because changes in ocean ridge activity do not occur quickly enough to give sedimentary cyclicity (i.e. on the order of <100000 years Golubic *et al.* 1979) and ice caps were absent in the Upper Triassic (Vail and Mitchum 1979). However changes in sea level by their very nature tend to effect large areas simultaneously (particularly on a shelf sea), thus it would not be unreasonable to propose that storm events during low sea level stands would be correlatable from place to place. As this is not the case in the Westbury Formation it is doubtful if eustatic sea level changes alone were the only factor controlling environmental energy levels. Thus more subtle, possibly long term climatic fluctuations may also have played a significant role. Einsele (1982) reviewing the effects of climatic variation pointed out that it influences:-

i) Water circulation patterns.

ii) Surface runoff from the land.

iii) The development of water column stratification.

Hence periods of extreme climatic variation maybe sufficient to cause reworking of sediments normally well beneath average, fair weather wave base, particularly when coinciding with slightly lowered sea level stands.

Long term climatic fluctuations are known to occur as a consequence of variations in the earth's tilt; these cycles have a periodicity of 21,000, 40,000 and 100,000 years and may effect long term sedimentary cyclicity as reviewed by Kerr (1981), Milankovitch (1941), Hays *et al.* (1976) and Imbrie and Imbrie (1979). In the context of the Westbury Formation, which was deposited over approximately 2 million years and contains up to nine limestone shale couplets, a simple calculation suggests a periodicity of approximately 200,000 years per couplet. Unfortunately

this figure does not obviously correlate with the "Milankovitch periodicity," however subsequent diagenetic processes may have obscured some of the cycles. Overall however within the confines of the current data set it is not known if "Milankovitch periodicicty" was important .

In conclusion Westbury Formation limestone/shale cyclicity was influenced both by diagenetic and sedimentary processes, and the sedimentary process were probably controlled by both climatic and subtle sea level variations. The overall effect was to cause cyclic deposition of dominant anoxic, organic-rich muds with interbedded, subordinate, oxic, coarser, clastic units.

Section 5.3. Controls on diagenetic style.

i) Diagenetic timing.

In order to understand the diagenetic processes that occurred in the Westbury Formation it is initially crucial to define them. Numerous authors (e.g. Larsen and Chillingar 1979, 1983) have discussed the nomenclature of diagenetic process and for the purposes of this study diagenesis is defined as:-

> "... the changes undergone by organic matter in the water column as well as all the chemical, physical and biological changes undergone by a sediment after its initial deposition (both) during and after its lithification, exclusive of surficial alteration (weathering) and up to pressures of 1 Kb."
>
> (Modified from Bates and Jackson 1983).

Having defined diagenesis it is also crucial to appreciate the timing of the different processes. Fairbridge (1983) in an attempt to place timing constraints on the different processes divided diagenesis into burial related "sub-stages". He suggested that the various processes could be divided into two stages; an early burial stage - syndiagenesis, where the initial reactions were controlled by their superadjacent pore water, and then later by bacteria and other subsurface organisms; and a deeper burial stage - anadiagenesis, where reactions are controlled by temperature. In this study labelling diagenetic process in this

manner was not considered useful, as it created extra jargon so labels were not used. Instead each process is discussed, the mechanisms controlling it reviewed and then broad temperature and depth constraints assigned.

ii) Physiochemical versus bacterial control of diagenesis in mudstones.

Mudstone diagenesis and the origin of nodular limestones within organic-rich muds has been the subject of considerable speculation by many authors notably Wobber (1965), Raiswell (1976), Irwin *et al.* (1977), Irwin (1980), Curtis (1977, 1980), Einsele (1982), Eder (1982), Ricken and Hemleben (1982) and Gluyas (1984). The models that these authors propose broadly divide into two groups:- those where diagenesis is considered to be under physiochemical control and those where diagenesis is under bacterial control, with the latter now considered to be at least initially the most important. Carbonate diagenesis in organic-rich mudrocks is very different to that in other carbonate sequences, notably reefs as reviewed by Longman (1980), Grover and Read (1983), Bathurst (1975) and Walkden and Berry (1984) where diagenesis is dominated by physiochemical effects.

The following section briefly reviews the physiochemical and biochemical processes that are most relevant to an appreciation of Westbury Formation diagenesis.

The dominant diagenetic effect observed in limestone shale sequences is usually the mobilization of carbonate. Carbonate mobilization occurs wherever the surrounding pore waters are in disequilibrium with respect to bicarbonate and calcium ions and the pH drops below 7.8 (Krumbein and Garrels 1952). Obviously carbonate precipitation occurs in the converse situation where there is an excess of bicarbonate and calcium ions and the pH is higher than 7.8.

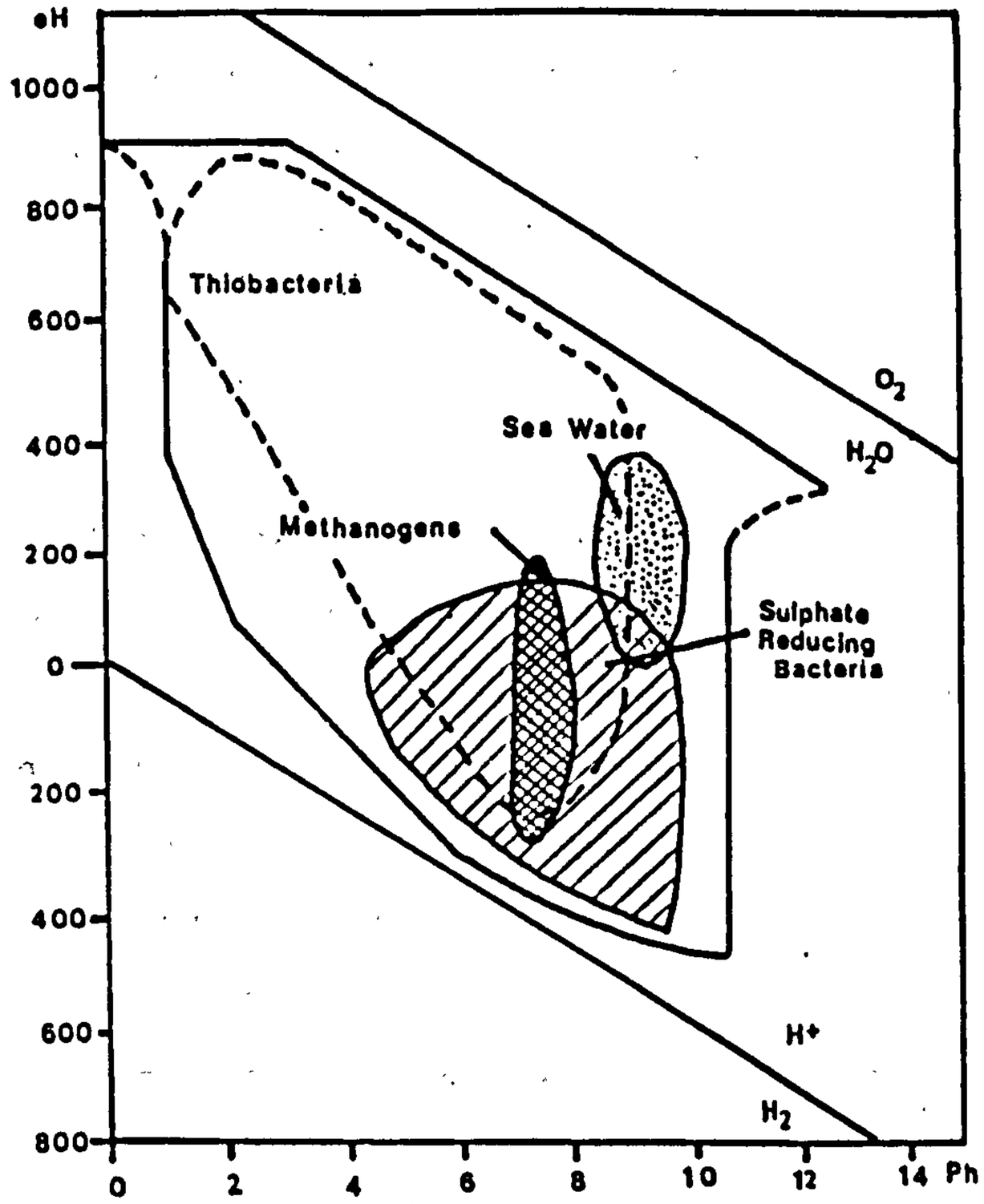
Einsele (1982) reviewed the processes where variations in global temperature and organic productivity altered the concentrations of dissolved ions in sea water, such that certain key changes in climatic conditions might cause the sea water to oscillate around carbonate equilibrium conditions, thereby causing limestone/shale cyclicity. Bjorlykke (1973) utilizing a variation of this model suggested that this was the mode of formation of Norwegian Lower Palaeozoic alternating nodular carbonates and shales.

Other authors notably Garrison and Kennedy (1977) have proposed that a homogenous sediment profile may rhythmically unmix as the metastable carbonates dissolve and are then reprecipitated at particular horizons. Einsele (1982) doubted that this process would occur, as he could not envisage a mechanism for causing random reprecipitation without a non-homogenous sediment profile.

Ricken and Hemblen (1982) provided examples from the Alps where pressure solution had cause local carbonate dissolution. The insoluble fraction was shown to have been concentrated on stylolite seams thereby producing limestone/shale alternations.

Micro-organism activity in sediments, particularly those that contain abundant organic matter may significantly alter the pH and Eh of the pore waters (figure 5.4). These changes may cause local carbonate dissolution and its reprecipitation elsewhere.

Figure 5.4. Catenary diagram showing the Eh and pH conditions associated with different bacterial groups and sea water (after Bass- Becking *et al.* 1960).



Irwin *et al.* (1977), Irwin (1980), Gluyas (1984) and Curtis (1977, 1980, 1983) proposed that bacteria were the dominant mechanism controlling carbonate equilibria in organic rich sediments. They clearly showed that in the Kimmeridge Clay, from isotopic evidence, the presence of pyrite and characteristic cement stratigraphies, that anoxic bacteria (notably sulphate reducers and methanogens) were the main controlling influence on early diagenetic processes. Raiswell (1976) postulated that similar bacterially mediated processes occurred in the Lias to produce the cemented units there.

The Westbury Formation mudstones contain huge quantities of pyrite, abundant biomarker evidence for bacteria (hopanes) and have similar cement stratigraphies to the Kimmeridge Clay. In the absence of significant pressure solution features, any evidence of "unmixing" (after Bjorlykke 1973) and sea water dissolution, it is probable that bacterially mediated diagenesis was the dominant process influencing the early burial of the Westbury Formation mudstones.

iii) Bacterial influences in sediments.

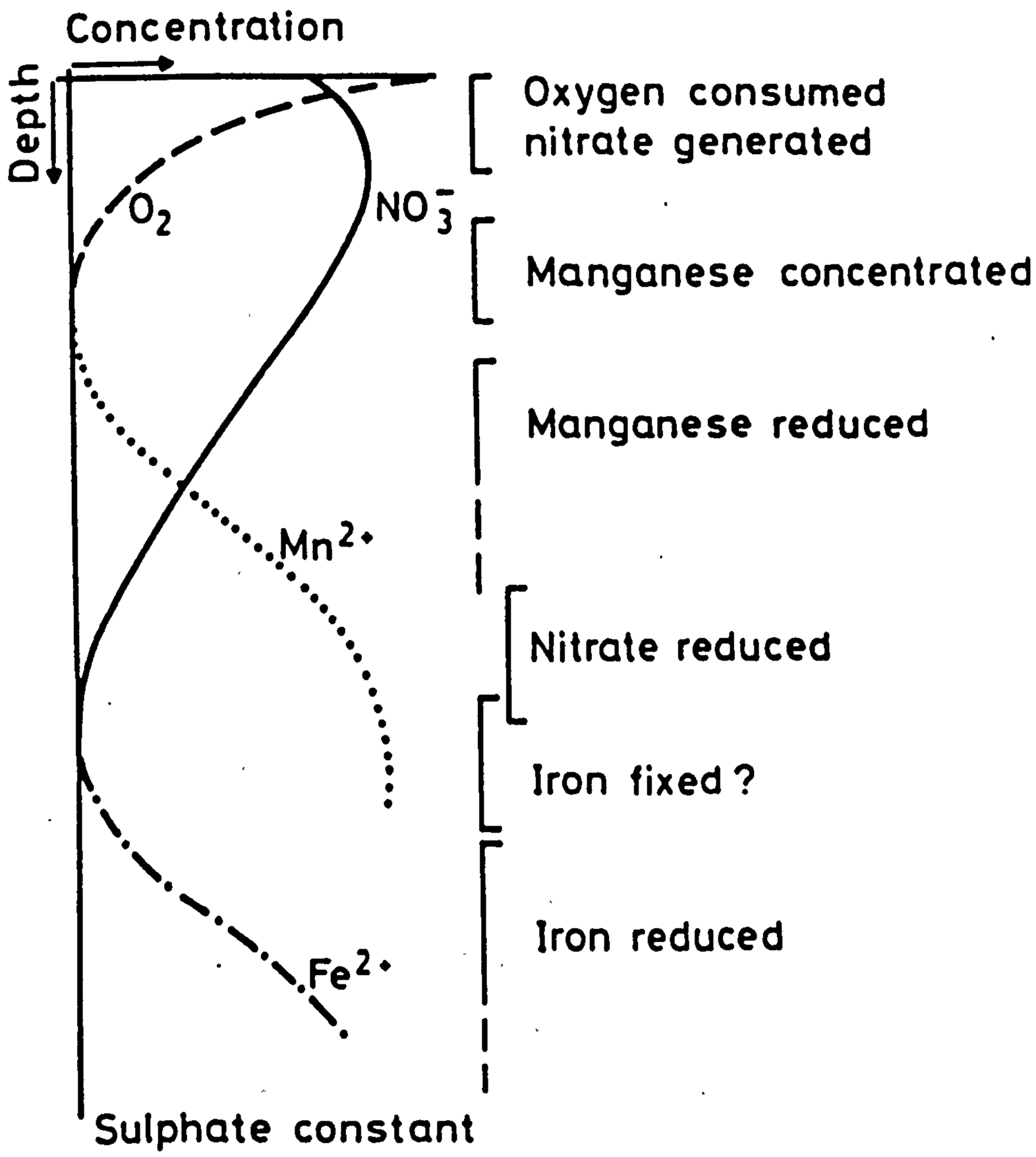
Having established that bacterial catabolism has significantly influenced many of the early diagenetic reactions present in the Westbury Formation, the possible effects of bacteria in sediments will be considered in detail.

a) Bacterial zonation in sediments.

Zobell and Anderson (1936) were the first to recognize microbial zonation in modern sediments. They showed that bacteria were common at shallow depths within all sediments. In a typical sediment profile they found that aerobic micro-organisms were abundant in the top few centimetres, beneath the aerobes, in anaerobic conditions they initially found sulphate reducers (particularly *Desulfovibrio sp.*) and then deeper in the profile they found methanogens. Emery and Rittenberg (1952) showed that the distribution of bacteria was roughly correlatable with the amount of buried organic matter and as burial increased so the number of organisms decreased.

Microbes utilize buried organic matter as electron donors (reducing agents) (Fenchel and Blackburn 1979) and dissolved nutrients as electron acceptors (oxidizing agents) (Brock 1979). Different nutrients make available to the organisms varying amounts of energy, hence organisms metabolizing with the most energy efficient nutrient (oxygen) will out compete those using less efficient nutrients (e.g. nitrate and sulphate) for suitable organic matter substrates (reducing agents) (Brock 1979, Fenchel and Blackburn 1979). Metabolic nutrients are normally only supplied by diffusion downwards from the water column (Goldhaber *et al.* 1977, Curtis 1977, 1980, 1983 and Mechlas 1974); as microbial metabolism depletes these nutrients a vertical zonation of bacteria and the different respiratory nutrients is set up in the sediment (figure 5.5 after Froelich *et al.* 1979).

Figure 5.5. The distribution of repiratory nutrients in a vertical sediment profile (Froelich *et al.* 1979).



Claypool and Kaplan (1974) pointed out that in marine sediments the two dominant respiratory nutrients are oxygen and dissolved sulphate. Thus in marine systems where there is abundant refractory organic matter, three micro-organism groups dominate the organic matter breakdown process:- aerobes, sulphate reducers and methanogens. However if the organic matter is less refractory, a more complete bacterial and nutrient profile develops where aerobes are followed by manganese reducers, nitrate reducers and finally iron reducers (assuming a constant supply of sulphate after Froelich *et al.* 1979) as sulphate reduction does not swamp the process.

The relationship between the different micro-organism groups is often very complex, as exemplified by the interaction between sulphate reducers and methanogens, and aerobes and anaerobes at the nutrient interfaces. These relations are further complicated by the presence of micro-environments in fine grained sediments, where aerobic and anaerobic conditions may exist in adjacent pore spaces (Postgate 1979) as a consequence of the limited diffusion in muds. The interaction between these different groups has been extensively studied by amongst others:- Martens and Berner (1974), Mechlas (1974), Barnes and Goldberg (1976), Warford (1979), Postgate (1979), Krumbein (1983), Jorgensen (1982, 1983), Pfennig and Widdel (1982) and Tuttle and Jannasch (1983). In general these authors found that the different groups and genera have different substrate requirements, and oxidize the organic matter with varying efficiency. They also found that some of the byproducts of metabolism were toxic to other micro-organism groups, notably hydrogen sulphide which is produced by sulphate reducers and is toxic to aerobes and at least some methanogens (Postgate 1979); thus methanogens and sulphate reducers are nearly always found at different levels of the sediment. This latter relationship may be enhanced by sulphate reducers being able to oxidize methane at the oxic/anoxic interface, thus creating an apparent separation of the two groups when in reality some methanogens are almost certainly able to tolerate high levels of hydrogen sulphide (Mechlas 1974, Raiswell 1986 pers. comm.). Further, the supply of methane at this boundary may significantly increase the activity of sulphate reducers (Raiswell 1986 pers. comm.).

The standard bacterial zonation scheme (i.e., aeroboes, sulphate reducers and methanogens) is disrupted by the juxtaposition of pore waters with high concentrations of different respiratory nutrients or sunlight. This is particularly significant where anoxic sediments with sulphate reducing pore waters are in contact with oxygenated pore waters. In these conditions the high concentrations of hydrogen sulphide restrict macrofaunal colonization of the sediment, but some groups (notably Thiobacteria) are able to oxidize the reduced sulphides using oxygen as an electron acceptor producing sulphuric acid (Jorgensen 1982). Related groups are also able (using light in an unusual photosynthetic process) to uptake carbon autotrophically in sulphide rich environments and in the process also produce sulphuric acid (after Jorgensen 1983).

It is worth noting that anoxia and particularly the presence of hydrogen sulphide does not necessarily exclude all macro-organisms from the sediment. Fenchel and Riedl (1970) and Schafer (1972) showed that some nematodes and bivalves were able to buffer its toxic effects, and survive at least for a limited period in sulphidic conditions. Recent research has also shown that some bivalves are able to thrive in anoxic conditions by using sulphate as an electron acceptor (Bosence pers. comm. 1986), or by living symbiotically with methanogenic bacteria (Suess pers. comm. 1985).

b) The effects of bacterial catabolism on modern pore water redox potentials, pH's and the concentration of some dissolved ions.

Berner (1966, 1968, 1968, 1969, 1971), Baas-Becking *et al.* (1960), Nissenbaum *et al.* (1972), Claypool and Kaplan (1974), Curtis (1977, 1978, 1980, 1983), Nedwell and Brown (1982), Krumbein (1983) and Jorgensen (1983) amongst many others have all studied the effects that bacterial catabolism, utilizing organic matter and various nutrients has on influencing pore water redox potentials, pH's and dissolved ion concentrations (figure 5.4).

In aerobic conditions organic matter is broken down by organisms using oxygen, after Nedwell and Brown (1982):-

$$CH_2O + O_2 + H_2O \longrightarrow CO_2 + H_2O$$

$$H_2O + CO_2 \longrightarrow H^+ + HCO3^-$$

Ammonia may also be released from the oxidation of proteins; phosphate from phospholipids and humic acids from the oxidation of terrestrial plant humin debris (Curtis 1977 and Berner 1969). The net result of all these processes is that the pH tends to drop (Berner (1969) (despite the presence of ammonia) and the amount of bicarbonate in the system rises (Curtis 1977).

During sulphate reduction organic matter is broken down by the sulphate reducers using dissolved sulphate as an electron acceptor. Using *Desulfovibrio sp.* the reaction may be summarized to (after Jorgensen 1983):-

$$2CH_3CHOHCOO + SO_4^{--} \longrightarrow 2CHCOO^- + 2CHCO_3^- + H_2S$$

Consequently the bicarbonate, hydrogen and hydrous sulphide ion levels in the pore water increases. Free hydrogen sulphide gas maybe released and unless the H_2S reacts to form pyrite, the Eh and pH will drop markedly. Ammonia, humic acids and phosphates may also be released from the organic matter.

In the methanogenic zone no inorganic electron acceptors are available, so organisms use complex molecules as oxidizing agents which they reduce to methane in a fermentation reaction after Curtis (1980):-

$$C_6H_{12}O_6 \longrightarrow 3CO_2 + 3CH_4.$$

Methanogens tend to decrease the redox potentials of the pore water and increase the concentration of bicarbonate ions.

The bacteria living at the main oxic/anoxic interface and in micro-environments are able to oxidize reduced sulphur compounds using both nitrate and oxygen as electron acceptors. This is reaction is observed in *Beggiota sp.* and in *Thiobacilli sp.* and is summarized as follows (Jorgensen 1982):-

$$2H_2S + O_2 \longrightarrow 2S^o + 2H_2O$$

$$2S^o + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4$$

Clearly sulphide oxidation may cause very low environmental pH's (see figure 5.4). A similar reaction is observed in phototrophic sulphide oxidizers (after Jorgensen 1983). They oxidize reduced sulphur compounds using light energy to obtain electrons:-

$$CO_2 + 2H_2S \longrightarrow (CH_2O) + 2S^o + H_2O$$

$$3CO_2 + 2S^o + 5H_2O \longrightarrow 3(CH_2O) + 2H_2SO_4$$

The effects of aerobic organisms, sulphate reducers and methanogens on pore water redox potentials is summarized in figure 5.4. Other micro-organism groups may also play a role in diagenesis, notably iron, nitrate and manganese reducers. The influence of these organisms is less well known and is documented in appendix 6.

Section 5.4. The influence of bacteria in the Westbury Formation.

i) Calcium carbonate dissolution, cementation and inversion.

Organic matter is oxidized to carbon dioxide by micro-organism catabolism (Curtis 1977, 1980); the carbon dioxide that is produced by this reaction may then dissolve in the pore water to form carbonic acid, thereby lowering the pH (figure 5.4). The early production of acidic pore water by this process may have caused the shell etching observed in the Westbury Formation calcareous sandstone facies. Conceivably this etching may have also been due to the carbonate being in disequilibrium with its associated pore waters in respect to its component ion concentrations, as a result of local changes in the amount of dissolved bicarbonate.

Jorgensen (1982) showed that very acidic pore waters are produced in modern sediments as a consequence of bacterially mediated sulphide oxidation producing sulphuric acid (figure 5.4) at the interface sulphidic/oxic environments and in photic/sulphidic environments. Inevitably if this process occurs carbonate

dissolution would follow. Sulphide oxidation may have significantly influenced the development of the Westbury Formation fossiliferous detrital mudstone facies as storms are believed to have aerated otherwise anaerobic/sulphidic sediments and in any case the bottom anoxic waters were often in the photic zone (where sulphidic, phototrophic anaerobes might thrive Krumbein and Cohen 1977). Sulphide oxidation may therefore be partly responsible for the early, extensive carbonate dissolution observed in the decalcified, detrital mudstone units. In this context dissolution may have been aided by the dissociation of hydrogen sulphide into its component ions with a consequent drop in pH. Storms have a "knock-on" effect, long after they have subsided as "oxic diffusion fronts" move through the anaerobic sediment (Thomson pers. comm. 1986). It is worth noting that carbonate dissolution may have also been caused by thermal decarboxylation (Curtis 1980) and/or organic acid production from the thermal maturation of organic matter (Carothers and Kharaka 1978 and Giles and Marshall 1986) during burial.

Locally within the Westbury Formation packstone units, the molluscan debris has been replaced by ferroan calcite. Which implies replacement must have occurred in iron rich pore waters - i.e., post sulphate reduction either within the methanogenic or the thermal decarboxylation zones. If precipitation had occurred in the sulphate reduction zone a non-ferroan calcite would have been expected, as a consequence of the reduced iron being preferentially incorporated into pyrite and not into the calcite.

Berner (1966) showed that carbonate dissolution occurred in some organic rich muds, as a consequence of lowered pH's associated with humic acid production. In the Westbury Formation this process was probably not significant as the organic matter is dominated by autochthonous algal organic debris which is relatively depleted in humic material.

In conclusion early carbonate dissolution in the Westbury Formation was due to a number of processes including:- aerobic oxidation, sulphate reduction, methanogenesis and sulphide oxidation. The temporal and spatial distribution of these processes was controlled by intermittent storm activity, burial rates, the diffusion of respiratory nutrients and water depth.

Carbonate precipitation occurs wherever the pore waters are supersaturated with respect to bicarbonate, suitable anion species are present and in alkaline conditions. Mechanisms that increase the pH in organic rich sediments and create conditions suitable for carbonate precipitation have been reviewed by many authors (e.g. Berner 1970, 1984, Irwin 1980, Curtis 1980 and Curtis and Coleman 1986). Iron reduction for instance increases the alkalinity of the pore waters:-

$$2Fe_2O_3 + CH_2O + 3H_2O \longrightarrow 4Fe^{++} + HCO_3^- + 7OH^-.$$

however where this reduction is associated with hydrogen sulphide production (i.e. in the sulphate reduction zone), this increase is offset by the dissociation of hydrogen sulphide into its component ions, unless hydrogen sulphide gas is able to escape from the sediment.

$$SO_4^{--} + 2CH_2O \longrightarrow HS^- + 2HCO_3 + H^+$$
$$(H^+ + HS^- \longrightarrow H_2S)$$

Iron reduction, where there is concomitant loss of H_2S may therefore trigger carbonate precipitation (Curtis 1980. Increased alkalinity is also caused by the breakdown of amino acids with the subsequent formation of ammonia (Berner 1968, 1969, Schafer 1972 and Irwin 1980). The oxidation of organic matter increases the pore water bicarbonate concentrations (Curtis 1977); thus where suitable anions exist carbonate precipitation may follow.

The availability of anion species is dependent on the chemistry of the prevailing pore water conditions and the minerals that are in equilibrium with them. The main control on these factors are:- burial depth, whether or not the pore waters are marine or freshwater, how much organic matter is buried with the sediment, the availability of nutrients for micro-organism metabolism and the availability of mineral oxidants e.g. iron oxides (Coleman 1985). In terms of the key ions for authigenic carbonate formation, calcite and phosphate are supersaturated with respect to sea water and Fe^{++} is available in reducing conditions. Given these criteria the carbonates that precipitate depend on the redox conditions of the pore water and which anions are present (Coleman 1985, Dreever 1982).

In the Westbury Formation there is a well developed cement stratigraphy with, non-ferroan bright luminescing cements associated with pyrite, followed by ferroan, dull luminescing cements. Clearly the ferroan cements were deposited in reducing conditions where there was Fe^{++} available to enter the calcite cement. The origin of the non-ferroan cements is potentially more problematic; obviously no Fe^{++} was available for incorporation into the cement; however may have been due to two very different reasons:- either the cements were precipitated in oxic conditions where there was no Fe^{++} available - or in reducing conditions where the Fe^{++} was being preferentially incorporated into pyrite.

As pyrite is present in association with the early non-ferroan cements and it is an efficient sink for Fe^{++} in sulphidic sediments, it is likely that the latter case prevailed. Thus the implication of this data is that initially cementation occurred in the sulphate reduction zone and latterly it occurred in the methanogenic zone (after Curtis 1977, 1980 1983 and Gluyas 1984). In both environments reducing conditions prevailed, organic matter degradation supplied the bicarbonate, sulphide was produced from sulphate reduction and the cations are available from sea water (summarized in figure 5.5). As there is no rhodochrosite or siderite in the Westbury Formation it is not known if other bacterial groups (other than sulphate reducers and methanogens) namely manganese reducers and iron reducers had any effect on carbonate precipitation. However as more than two cement zones are often observed it is tempting to speculate that these other groups may have influenced cementation.

Cement precipitation in the Westbury Formation occurs in two distinct styles. First as drusy, zoned carbonates that infill primary shelter porosity, within the lithoclastic packstones. Secondly as microsparry calcites filling intraparticle porosity in the wackestones.

The former precipitated on pre-existing nuclei and grew into shelter porosity where the bulk of the sediment was composed of carbonate debris, whilst the latter formed where the bicarbonate concentrations in the pore waters were supersaturated and nucleation occurred at many discrete sites within a detrital mudstone unit.

It is doubtful if in the Westbury Formation any of the cements present were formed in the aerobic zone, as the earliest examples are bright luminescing and non-ferroan. Cements forming in oxic conditions would be expected to have non-ferroan, dull luminescing characteristics as a consequence of the calcite excluding ferric iron and the lack of incorporation of Mn^{++} into the lattice (Carpenter and Oglesby 1976).

In the Westbury Formation metastable aragonite and high magnesian calcite has inverted to calcite. This neomorphic process has produced pseudopleochroic textures in bivalves which often have ghosted outlines; and has also recrystallized the micrite, leaving relict micrite patches in the pseudospar. Inversion has caused the microspar and allochems to exhibit even, undifferentiated luminescent characteristics. These neomorphic fabrics did not develop from earlier cements because they show no remnant zonation, as described by Bathurst (1983). As well defined pseudopleochroic fabrics are preserved locally it is likely that recrystallization occurred relatively quickly (Hudson 1962 and Sandberg and Hudson 1983). Recrystallization occurs where metastable carbonates are placed in disequilibrium with their surrounding pore waters (Berner 1966). Bathurst (1975) noted that recrystallization often occurred in organic rich sediments. Folk (1974) argued that this may be due to freshwater flushing of marine pore systems, whilst Fryle and Bischoff (1965) proposed that high concentrations of dissolved sulphate may have a similar effect. As there is no evidence of freshwater flushing it can only be assumed that the high concentrations of dissolved sulphur species caused this recrystallization.

ii) Phosphate formation.

The presence of abundant phosphates in the Westbury Formation has also engendered much speculation. Previous workers (Richardson 1901, Arkell 1933) have assumed that the formation of "bone-beds" was a consequence of reduced sedimentation rates, with the abundant phosphates either being derived from mass mortality events (Jukes Brown 1892, Short 1904, Reynolds 1947) or from strand line lag concentrations (Hamilton 1977, Mayall 1979) which had reworked underlying

sediments. In the context of the Westbury Formation it is clear that reworking of bone material has occurred as the skeletal elements are disarticulated and scattered. This could arise for two reasons:- post-mortem refloating and scattering of carcasses (after Schaffer 1972) and/or sediment reworking by storms. On the abundant evidence of storm activity it is probable that scattering was at least in part caused by storms.

It is worth considering if mass mortality events contributed to the formation of these "bone-beds". There is certainly (particularly in the Worcester Graben) evidence of abundant dinoflagellates in the Westbury Formation, which may indicate that there were phytoplankton blooms and possibly water column anoxia. Whilst this is an interesting observation it is does not necessarily imply that mass mortality occurred.

The Westbury Formation calcarenaceous sandstones locally contain abundant coprolitic debris and abraded bone material. As it is unlikely that unaltered coprolites would survive storm reworking, the wear patterns on the fish scales show abrasion (Mayall 1979), there is no evidence of exotic mineralization and some evidence of phosphatic zonation it is likely that inorganic francolite precipitation occurred within the organic phosphatic nuclei. The inorganic enrichment of the primary organic nucleus would hardened the relatively soft matrix allowing it to be reworked and still recognisable. This process has been described by Reif (1971, 1976) and termed "pre-fossilization". Precipitation of francolite in the Westbury Formation necessarily demands that the pore waters, albeit locally must have been supersaturated with respect to dissolved phosphate and bicarbonate ions implying specific redox conditions (Krumbein and Garrels 1952).

The geochemistry of Recent phosphate deposits and phosphate precipitation has been extensively researched by Kazakov (1937), Gulbrandsen (1969), McConell (1972), Cook (1976), Burnett (1977), Riggs (1979), Cook and McElhinny (1979), Bremner (1980), Burnett (1980), Notholt (1980) and Baturin (1982). Phosphate

is the main limiting resource for organic productivity in marine systems (Cook 1976) as it is a vital component of some body armour, skeletal materials, and all nucleic acids and phospholipids (Riggs 1979). Normally phosphate is recycled by organisms from phospholipids and nucleic acids and does not build up in sufficient concentrations in the pore waters to precipitate as a cement (Froelich *et al.* 1979). However where there is increased organic productivity in the surface layers and bottom water anoxia, excess phosphate is incorporated into the sediment and not recycled due to the reduced organic activity (Cook 1976). High concentrations of phosphate in the surface waters are a pre-requisite for increased surface productivity and this is usually associated with volcanic exhalations, guano deposits, marine upwelling or reworking of previous phosphorite deposits (Cook 1976). In the Westbury Formation there is little evidence that any of these processes supplied the initial high concentrations of phosphate, thus it can only be assumed that this phosphate was derived from terrestrial runoff.

Phosphate is initially incorporated into the sediment complexed on clays, within organic matter and as ferric phosphates (Berner 1973). In the anoxic reducing conditions associated with early burial in organic rich muds, this phosphate is liberated by the anaerobic oxidation of organic matter by bacteria and by the reduction of clays and ferric phosphates. This liberation causes the pore waters to become supersaturated with respect to francolite. Where the pH is lower than 7 - 7.8 (the calcite stability field) phosphate will precipitate on pre-existing phosphatic nuclei (Krumbein and Garrels 1952). Obviously the bicarbonate and calcium ions will be derived from the dissolution of calcite and oxidation of organic matter.

Oxidized phosphate is very stable in most marine systems (Fenchel and Blackburn 1979); reduced phosphate which is highly toxic has not been found in modern marine sediments. Despite this Trudinger (1976) postulated that reduced phosphate species might be suitable electron acceptors (i.e., oxidizing agents) for some specialised bacterial groups. This being the case reduced phosphate would be available at oxic/anoxic interfaces for phosphate precipitation. Unfortunately this process has never been observed (Trudinger 1976) and is probably irrelevant as far as the Westbury Formation is concerned.

Phosphate precipitation in the Westbury Formation was a consequence of increased surface productivity, which supplied excess organic matter to the sediment and caused sediment and possibly bottom water anoxia. The phosphate in the sediment was then remobilized and not fully recycled by organisms, thus phosphate concentrations in the pore waters rose. Finally as a consequence of the localized reducing conditions and lowered pH's (as a result of bacterial catabolism) francolite preferentially precipitated with respect to calcite on pre-existing nuclei to enhance "bone" preservation. Subsequent storm processes are then envisaged as having reworked the phosphatic material into "bone-beds".

iii) Pyrite formation.

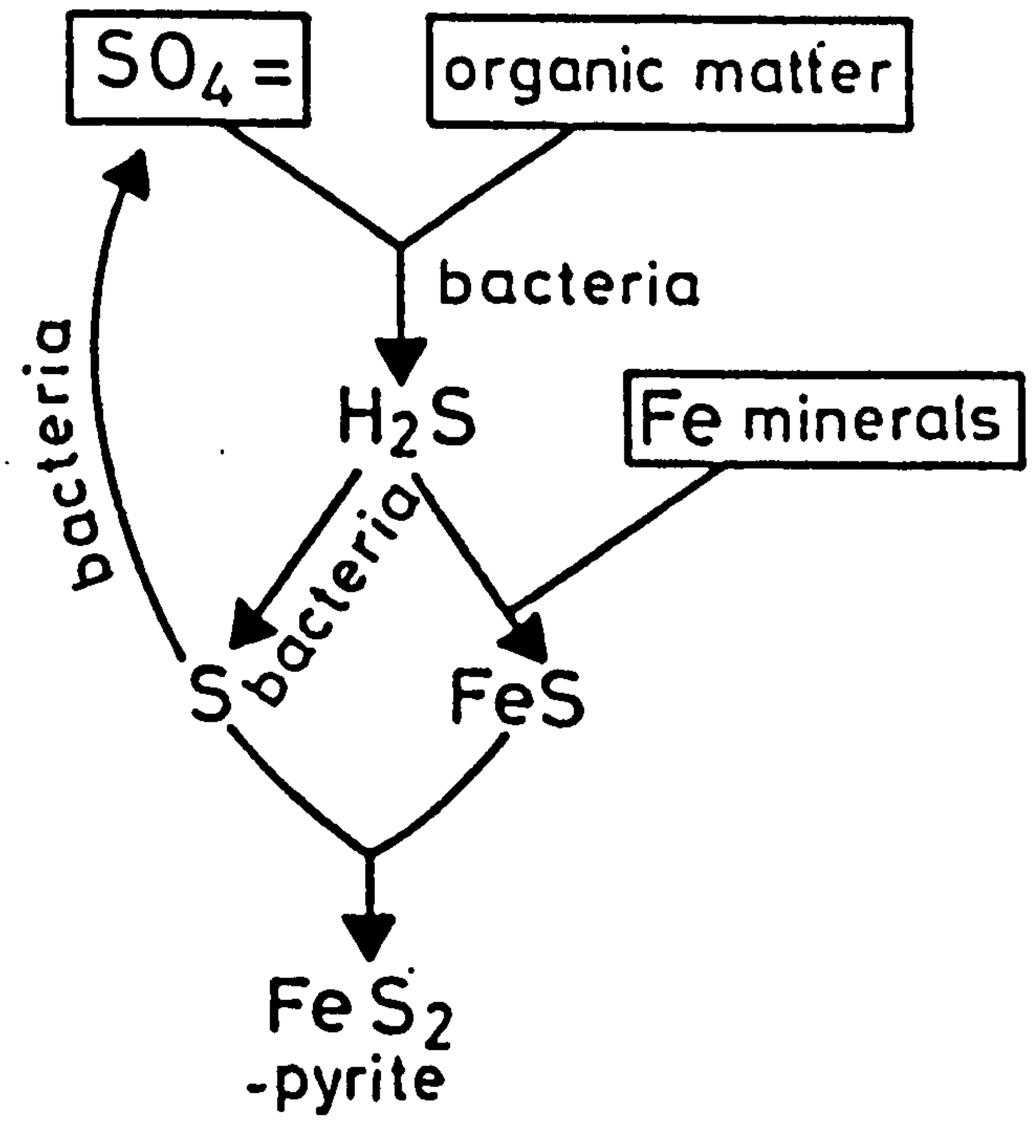
Pyrite is present in all of the Westbury Formation facies both as euhedral and as disseminated crystals. Pyrite formation has been extensively reviewed by Berner (1970, 1984) who showed that it formed in the sulphate reduction zone as a consequence of the reaction of biogenic hydrogen sulphide and oxidized iron species to initially form iron monosulphides and then to react with elemental sulphur to form pyrite (figure 5.7). The overall reaction maybe summarized as:-

$$2CH_2O + SO4^{--} \longrightarrow H_2S + 2HCO^{---}$$

Curtis (1980) postulated that the oxidized iron for this reaction may derive from soil sesquioxides, whilst Irwin (1980) proposed that it derived from haem rich organic matter and Elderfield (1977) suggested that it may derive form iron rich detrital clays. Either way iron in mud rocks is rarely a limiting factor to pyrite formation, and pyrite will continue to form in the sediment as long as sulphides are available i.e., within the sulphate reduction zone (Berner 1984).

There is no reason to assume that Westbury Formation pyrite formed in any other way than in the sulphate reduction zone as a consequence of hydrogen sulphide reacting with reduced iron species.

Figure 5.6. A cartoon of idealized pyrite formation (Berner 1984).



iv) The formation of authigenic silicates.

One of the earliest diagenetic phases preserved in the Westbury Formation is K feldspar overgrowths around etched detrital K feldspar grains. The early etching of the K-feldspars implies that the pore waters were initially unsaturated with respect to K^+, SiO_2, Al^{+++} and O_2, and then as equilibrium conditions returned an authigenic K feldspar phase was reprecipitated. Kastner (1971) recognized that the prerequisite ions for K feldspar growth could most easily be obtained from other silicates, notably illites, chlorites, other detrital feldspars and in the case of potassium sea water. K feldspars are stable in alkaline conditions with high K^+ and SiO_2 ion activity (Garrels and Christ 1965, Kastner 1971). Authigenic growth of K-feldspars in the Westbury Formation was

initially coupled with lowered pH, which may have been associated either with sulphide oxidation or excess aerobic catabolism; in any case acidic pore waters probably provided the necessary ions for subsequent K feldspar precipitation which followed when alkaline conditions with high K^+ activity returned (either in aerobic conditions with increased bicarbonate concentrations or during early sulphate reduction). As quartz etching has not been observed it is unlikely that the pH ever rose above 8.5 (Garrels and Christ 1965).

Elderfield (1977) suggested that coupled with the neomorphic inversion of metastable carbonates and the concomitant release of magnesium ions to the pore waters a magnesium rich clay assemblage might form. Contrary to this Bathurst (1975) suggested that the excess Mg^{++} ions might be incorporated into dolomite. This process Elderfield (1977) argued would be enhanced by reducing, sulphidic conditions, where iron rich detrital clays would undergo cation exchange with magnesium, to form a magnesium rich authigenic clay assemblage and pyrite:-

$$Fe^{++} - Clay + Mg^{++} \longrightarrow Mg^{++} - Clay + FeS_2$$

In Elderfield's (1977) opinion this process would also contribute Fe(II) for subsequent pyrite formation. However Heller-Kellai and Rozenson (1978) refuted this mechanism pointing out that iron is structurally bound within the clay lattice and cation substitution would cause lattice destruction.

The Westbury Formation does not contain an authigenic magnesium rich clay assemblage in the less than 2 micron fraction, nor does it contain authigenic dolomites. This therefore agrees with Jeans' (1978) assertion that an authigenic Mg^{++} rich clay assemblage is absent, which in his opinion was a consequence of marine rather than hypersaline depositional conditions, and it suggests that iron rich clays were not undergoing cation exchange with Mg. Unfortunately the <0.5 um. clay fraction was not analysed.

v) Bacterial diagenesis and organic biomarkers.

The abundant hopanoid component in all the Westbury Formation samples indicate that bacteria significantly modified the autochthonous algal and terrestrial organic matter. The pristane/phytane (pr/ph) ratios indicate slight variations in sediment and water column anoxia, with the Worcester Graben samples showing higher pr/ph ratios, implying that they were being oxidized in sulphate reducing conditions for a greater time compared with the Bristol Channel Trough samples (after Didyck *et al.* 1978); which in this context probably means that they spent less time in the oxic parts of the water column. The higher hopanoid/steroid ratios in the Bristol Channel Trough intuitively support this proposal, as hopanoids are an important constituent of bacteria (e.g. Ourisson *et al.* 1979, Brassell *et al.* 1981), their abundance indicates increased bacterial contribution to the organic matter in this latter basin. The unusually high phytane component in the Stowell Park sample (figure 3.10) suggests that it may have a significant input from archaebacterial lipids e.g. methanogens (Holzer *et al.* 1979). Most of the bacterially influenced diagenesis of the organic matter in the Westbury Formation probably occurred in anoxic parts of the water column and in the sulphate reduction and methanogenic zones.

Section 5.5. Physiochemical diagenesis in the Westbury Formation.

i) The generation of acidic pore waters by physiochemical processes during burial.

As the organic matter in muds is heated carbon dioxide is driven off in a process termed thermal decarboxylation, this CO_2 is then available to react with the pore water to lower the pH, possibly as low as pH 3 (figure 5.7) (Curtis 1983). Obviously this may cause carbonate and possibly clay dissolution during burial and may have contributed to shell dissolution in the Westbury Formation.

It has also been noted, particularly in oil field waters that the pore water may contain appreciable quantities of organic acids (Carothers and Kharaka 1978). These acids are derived from the maturation of the organic matter and potentially may leach carbonate minerals (Surdam *et al.* 1984). It is worth noting that the Westbury Formation muds have not generated any oil and thus this process is not likely to be important in this context as a source of acidic pore waters.

Generation of acid pore waters during burial is important as the ions that are produced during the dissolution of unstable minerals can contribute to the formation of other authigenic phases (see below).

ii) Cone-in-cone formation.

Cone-in-cone calcite has been recorded from the Westbury Formation by many authors including:- Richardson (1911) and Whittaker and Green (1983). In this study it was frequently encountered associated with the carbonate units, and often (particularly in the Bristol Channel Trough) with intense dissolution and recrystallization of the metastable fossils. In the Westbury Formation cone-in-cone carbonates are composed of non-ferroan, dull luminescing calcite and often contain pyrite inclusions.

Marshall (1982) reviewing earlier work noted that cone-in-cone carbonates were of diagenetic origin. He proposed, using isotopic evidence that the ions for their formation were derived from the dissolution of metastable fossils, whilst Irwin *et al.* (1977) had suggested that cone-in-cone formation was triggered by shale decarboxylation.

In the Bristol Channel Trough cone-in-cone and intense dissolution fabrics are present; whilst in the Worcester Graben these textures are rare, although neomorphic fabricss are common. Assuming Marshall's (1982) assertion is correct (that the ions for cone-in-cone formation are derived from the mobilization of aragonitic material), it is postulated that the Worcester Graben metastable

carbonates recrystallized sufficiently early to prevent subsequent dissolution supplying ions for later cone-in-cone growth. In the Bristol Channel Trough however, early neomorphic transformations were not so intense. As a result metastable fossils were preserved, and their subsequent dissolution supplied ions for cone-in-cone formation. Hence an inverse relationship exists between the presence of intense neomorphic fabrics, and poor cone-in-cone development in the Worcester Graben, and between less recrystallization with well developed cone-in-cone formation in the Bristol Channel Trough. Which implies that initial sediment anoxia influenced later cone-in-cone formation, assuming that the concentration of dissolved sulphate ions controlled the neomorphic transformations (after Fryle and Bischoff 1965). It is of course worth noting that calcite dissolution may have been triggered by acidic pore waters generated during thermal decarboxylation or as a consequence of organic acid production during thermal maturation of the organic matter (after Carothers and Kharaka 1978), in which case both processes would have been greater in the Bristol Channel Trough as it has been buried deeper.

The fact that the Westbury Formation cone-in-cone calcites are composed of non-ferroan, dull luminescing carbonates and contain included pyrite grains (which were incorporated into the fabric long after they had formed), suggests that they formed in post aerobic conditions, probably in the late sulphidic, methanogenic or thermal decarboxylation zones. That no manganese or iron was incorporated into the calcite lattice suggests that these ions were either swept aside by the slow rate of crystallization or that they were incorporated into other phases.

Cone-in-cone fabrics are formed in over-pressured sediments and tend to precipitate on pre-existing nuclei (i.e., cemented units), particularly along pore water migration paths (Raiswell 1971). In the Westbury Formation, dissolution of biogenic carbonates within the shales probably supplied the dissolved ions for cementation. As the organic matter maturation indices (hopane and sterane isomerization) indicate that the Westbury Formation has only been buried to shallow depths, it

is unlikely that the illite/smectite transformation to illite (Hower 1981) supplied sufficient water for overpressuring. Overpressuring in this context must therefore have been due to sediment compaction and concomitant expulsion of depositional pore waters. It is also worth noting that the redox potentials of the expelled pore water may have reflected a bacterial catabolic process, particularly methanogenesis, and thus may have been acidic.

Overall the Westbury Formation cone-in-cone fabrics are assumed to have formed in excess of 100 metres, in the late methanogenic or decarboxylation zones, but not at depths in excess of 3 kilometres.

iii) Clay mineral transformations.

The association between K-feldspar dissolution and authigenic illite and illite smectite formation, is well documented in burial diagenetic systems (Reynolds and Hower 1970, Brindley and Brown 1980, Hower *et al.* 1976, Hower 1981, Ali and Turner 1982), particularly from samples from the Gulf Coast. As burial progresses these authors found that the amount of K-feldspar decreases whilst the amount of illite/smectite and illite increases; these are a consequence of the mobilization of the potassium in slightly acidic conditions. Whole rock, X.R.D. and petrographic analysis of Westbury Formation samples has revealed abundant feldspars with unetched authigenic overgrowths in the sandstone and calcarenaceous sandstone facies, and a very poorly developed "mixed-layer" authigenic illite/smectite mixed layer phase in the detrital mudstones (appendix 3). With about 40% illite in the illite/smectite phase, using the criteria of Hower (1981), (note the cautionary comments of Nadeau *et al.* (1984)). This implies that during early deposition of the calcareous sandstone and calcarenaceous sandstone facies, equilibrium conditions prevailed which favoured clay dissolution (particularly detrital illite), at the expense of K-feldspar precipitation and that later, during burial there was only minimal redistribution of potassium forming the authigenic illite/smectite phase. This implies that during early burial there was considerable silicon and potassium ion activity in alkaline pore waters, at low temperatures and pressures (Kastner 1971) and that later burial did little to mask this process.

iv) Thermal alteration of organic matter preserved in the Westbury Formation.

The organic matter maturity indicators preserved in the Westbury Formation, indicate that the two depositional basins have had slightly different thermal histories. The organic matter in the Bristol Channel Trough has significantly lower CPI (carbon preference index) values (table 4.1), has a higher diasterene/diasterane ratio (table 4.1), has only 4α-methylsteranes (rather than 4α- and 4β-methylsteranes), contains 17β(H), 21β(H)-hopane (rather than 17α(H), 21β(H)-hopanes and 17β(H), 21α(H)-hopanes) and a more similar proportion of 20S and 20R isomers in the C27 - C29 steranes) compared to the Worcester Graben samples. Which indicates that the Worcester Graben samples are less mature than those from the Bristol Channel Trough (Mackenzie *et al.* 1980, 1982, Tissot and Welte 1984, Wolff *et al.* 1985), and that neither has reached the oil generation threshold (Macquaker *et al.* 1985) as indicated particularly by the absence of 14β(H), 17β(H)-steranes (Mackenzie *et al.* 1980).

CHAPTER 6

A SUMMARY OF THE DEPOSITIONAL AND DIAGENETIC HISTORY OF THE WESTBURY FORMATION.

Section 6.1.

The Westbury Formation in south west Britain was deposited in two tectonic basins, the Bristol Channel Trough and the Worcester Graben. Sedimentation occurred in a shallow marine, stratified, shelf sea on a blind arm of Tethys, which was not influenced directly by oceanic circulation patterns. The surface waters were very productive as a result of abundant nutrient input from nearby land and as a consequence of storm recycling of nutrients. Abundant surface productivity caused the bottom waters to become anoxic and sulphidic as a result of excessive aerobic decay processes.

During depostion of the Westbury Formation ambient energy conditions were generally low, although high energy episodic storms (probably hurricanes) did occur. During low energy periods the main clastic input was detrital, silt grade quartz and K feldspars and a detrital illite, kaolinite clay assemblage. As a consequence of high surface phytoplankton productivity the bottom waters became anoxic (particularly in the Worcester Graben) and much autochthonous organic matter was incorporated into the sediment (dominated by algal and dinoflagellate derived organic matter). The organic matter which had partially been oxidized in the water column by aerobes (particularly in the Bristol Channel Trough) was subsequently broken down by sulphate reducers and methanogens in the sediment. This caused the formation of abundant authigenic pyrite and left the organic matter with significant bacterial biomarker components notably, abundant hopanes and phytane.

During periods of storm activity, coarser detrital debris was carried into the basins including sand grade quartz, K feldspars and biogenic carbonate debris. Storm waves formed to a varying extent symmetrical ripple

lamination, spill over ripples, rip up cobble clasts, gutter casts, graded rhythmites, and aligned many of the biogenic carbonates, causing them to be preserved convex up and often end-on. They also briefly oxygenated the sediment which allowed macrofaunal colonization and this resulted in some of the storm units being intensely bioturbated. In spite of this return to normal marine bottom water conditions, the fauna is dominated by opportunistic bivalves, with some local development of algal and bacterial mats, as conditions were not stable for long enough to develop a mature community. During the storms aerobic respiration caused the pore waters to become initially acidic which partially etched some of the calcareous bioclasts and detrital K feldspar grains.

The presence of oxygen in predominantly anoxic sediments caused aerobic/anaerobic interface environments to develop which were ideal for sulphide oxidizing bacteria. Their metabolism resulted in very low pore water pH, which consequently caused major dissolution of the metastable carbonates and clays. This caused complete decalcification of some of the carbonate units and resulted in the preferential preservation of phosphatic debris, as the increased bicarbonate and phosphate concentrations in the pore waters caused inorganic phospate precipitation. Subsequent storms then reworked and concentrated this phosphatic material. Interface redox conditons may also have been responsible for glauconite formation.

With the re-establishment of low energy conditions oxygen demand (via aerobic organisms) exceeded oxygen supply and the bottom water and sediment became anoxic and sulphidic (via sulphate reduction). Coupled with this the pore water bicarbonate concentrations rose and potassium ion activity increased (as a consequence of detrital clay dissolution). Consequently authigenic K feldspar overgrowths precipitated on the detrital K feldspar grains and local calcite cement precipitation occurred in the storm units. The earliest calcite cements to precipitate were non-ferroan and were formed in the sulphate reduction zone where bacteria supplied H_2S to mop up the available Fe(II) forming pyrite. Whilst the later calcite cements were ferroan and precipitated in the methanogenic zone where sulphides were not available to mop up the excess Fe(II).

Locally microsparry non-ferroan nodular calcites precipitated in the shales where there was no previous carbonate nuclei. The high concentrations of dissolved sulphates, sulphides and organic matter caused the metastable carbonates to invert to low magnesian calcite and the lime muds to recrystallize (particularly in the Worcester Graben) forming pseudopleochroic textures and floating micrite textures. Bacterial related diagenetic processes were brought to a close with increasing burial and higher temperature.

The burial diagenetic processes that followed included:- the formation of mixed layer illite/smectite phases, thermal decarboxylation, the formation of cone-in-cone calcites and the modification of the organic matter. The mixed layer illite/smectites are poorly developed and are not a significant component. Cone-in-cone carbonates are however locally well developed (particularly in the Bristol Channel Trough) and are associated with shale dewatering and the dissolution of metastable carbonates. Cone-in-cone calcites have formed particularly on the previously cemented carbonate units and these acted as a barrier to dewatering, and are common where metastable carbonates have survived the bacterially related neomorphic changes. Burial diagenesis also effected the organic matter, particularly in the Bristol Channel Trough (which reached higher temperatures than the Worcester Graben), where there are only 4-methylsteranes, the diasterne/diasterane ratio is higher, and the hopanoids and steroids have higher temperature isomers. Despite this neither basin has been buried deep enough to generate oil.

The Westbury Formation in south-west Britain is thus a classic black shale sequence. It exhibits all the common features of bacterially influenced diagenesis and as it was deposited in the photic zone, was occasionally disrupted by storms it has in addition well developed storm fabrics and, unusually, interface oxic/anoxic micro-environments. A summary diagram of the diagenetic scheme is presented in figure 6.1, whilsts the early diagenetic process are placed in context within a sedimentary profile in figure 6.2 and a palaeoecological reconstruction is given in figure 6.3.

Figure 6.1. Cartoon of the diagenetic events in the Westbury Foramtion, showing the timing of each process and the diagentic zone in which it occurs (O_2 oxic zone, $SO_4^=$ sulphate reduction, CH_4 methanogenic and thermal decarboxylation zones.).

	MAIN SEDIMENT ZONES				
PROCESSES	O_2	$O_2/SO_4^=$	$SO_4^=$	CH_4	CH_4
K FELDSPAR PPT.	◄■■■■►				
PHOSPHATE PPT.	◄■■■■►				
CLAY DISSN.	◄□□□□►				
NFC. CEMENTATION		◄■■■■■►			◄■■■►
ARAGONITE INV.		◄□□□□►			
PYRITIZATION		◄■■■■■►			
CARBONATE DISSN.	◄□□□□►			◄□□►	
FC. CEMENTATION			◄■■■■■►		

■■—Cementation.

□□—Dissolution.

Figure 6.2. The main factors influencing early diagenesis in the Westbury Formation. Showing the influence of light and wave activity on bacterial zonation and the main reactions these cause.

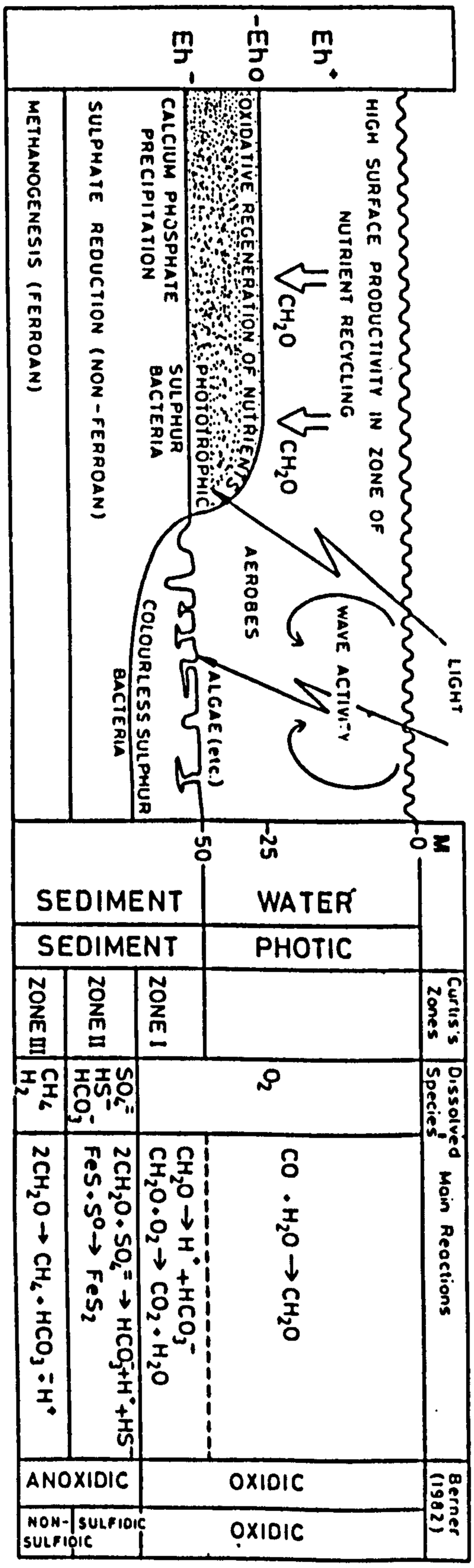
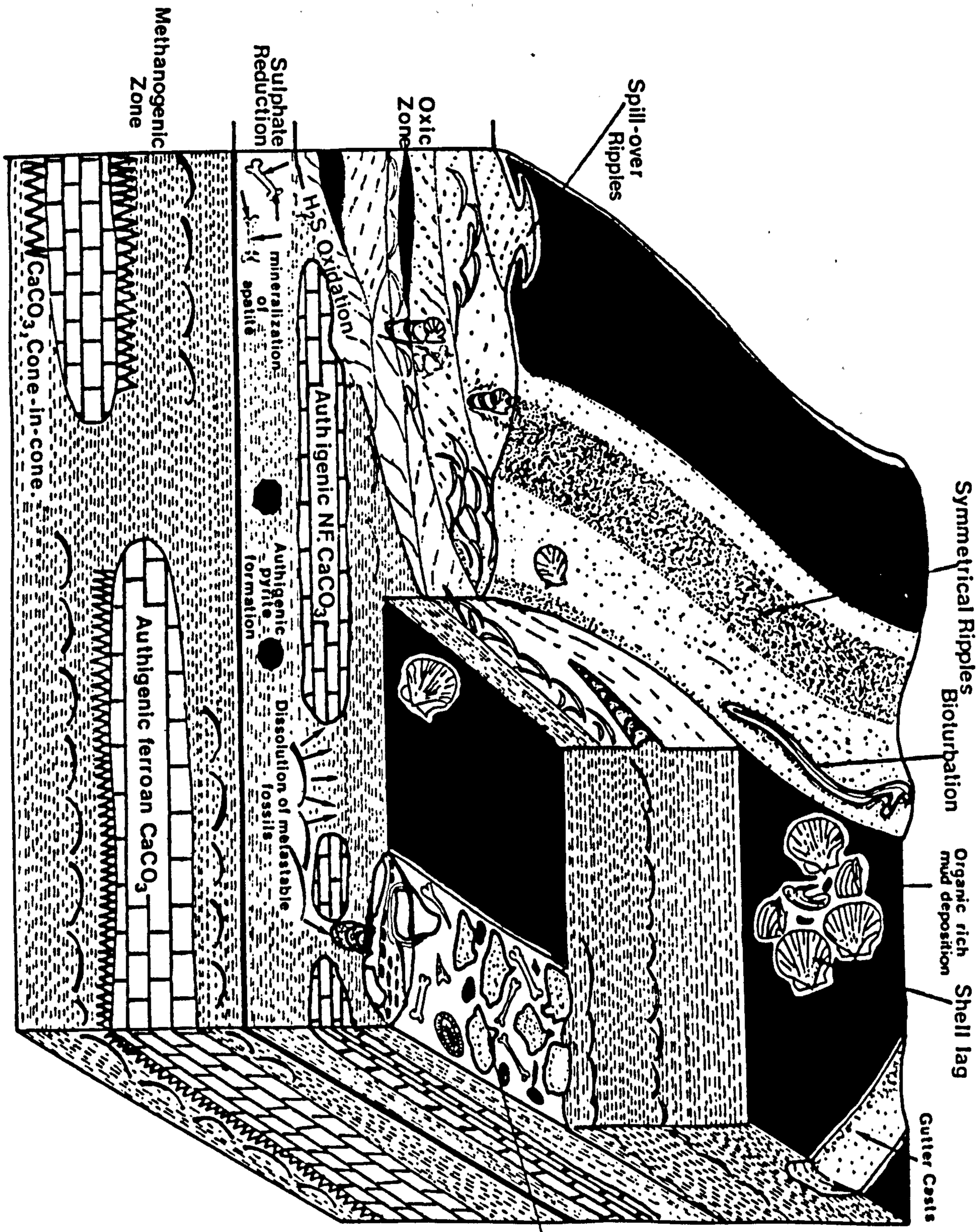


Figure 6.3. A summary of the sedimentary (ripple formation shell lag development etc.) and diagenetic (carbonate, apatite and pyrite precipitation) processes, occuring in the Westbury Formation showing the interaction between organisms and their environment the effects of sedimentary cyclicity (organic rich-mud/carbonate units). Further the diagram shows the effects of the variable availability of respiratory nutrients (notably oxygen and sulphate) on the development of the diagenetic profile and where these processes occur.



Section 6.2. Concluding remarks.

Future research should concentrate on diagenetic aspects of the Westbury Formation. Specifically, the origin of the complex calcite cements should be established, using laser sampling techniques to examine their stable isotopic signature, to determine if other bacterial groups were significant (particularly methane oxidizers). Similar analytical techniques should also be used on the calcite cone-in-cone structures. Further, detailed investigation of the organic matter using GC-MS would be useful, especially if coupled with analysis of its stable isotopic signature. Detailed inorganic geochemistry of the clays would probably not be useful as the Westbury Formation in the study area had not reached significant temperatures and it had not generated oil. Further, back scatter electron microscopic analysis may provide interesting data of elemental distribution in the shales, particularly that associated with pyrite formation, cone-in-cone formation and the mobilization of carbonate in the shales. As the current published models of black shale diagenesis only concentrate on the effects of sulphate reducers and methanogens, further research should be undertaken on the influence of other bacterial groups on this process, particularly in the light of this study, where sulphide oxidizers may have played a significant role.

APPENDIX 1. Literature Review.

It is not intended to provide an exhaustive review of the voluminous Rhaetian literature however, a few key references will be discussed. A reader requiring more detail is directed to:- Ivimey-Cook (1962), Bazley (1968), Mayall (1979), Duffin (1980), Warrington *et al.* (1980) and Jones (1981).

The "Rhaetic" was first proposed as a stage name in southern Europe by Oppel (1858), with reference to the alternating marl/limestone, marine sediments that post dated continental sedimentation of the Keuper. Wright (1858) was the first to recognise that the "Westbury Beds" in Britain were of "Rhaetic" age. Moore (1861) described their fauna and (Moore 1867) speculated that they were deposited "slowly" in "peculiar oceanic" conditions. Etheridge (1865) described "bone-beds" in the "Westbury Beds" and suggested that they were correlatable over large areas and were significant time horizons as they were formed by mass extinction events. Generally the "bone-beds" were considered to mark the end of Triassic continental conditions and the onset of Jurassic marine deposition.

In the latter part of the nineteenth century, little further environmental speculation was undertaken with respect to the "Rhaetic"; the papers that were published, mainly confined themselves to documenting temporary exposures, and arguing further about the formation of "bone-beds". Davis (1881) for instance, suggested that "bone-beds" were formed as a remanie deposit, a suggestion which was disputed by Winwood (1881) on the basis that the bones were not water worn and he preferred Etheridge's (1865) earlier mass extinction model.

During the early years of the twentieth century "Rhaetic" research was dominated by Richardson in numerous papers (Richardson 1901, 1903, 1904, 1904, 1905, 1905, 1906, 1911 and 1933). He documented on a county to county basis all the Rhaetian exposures and produced the first palaeogeographical reconstructions (Richardson 1901). He proposed that most

of south west Britain was flooded, with the exception of minor islands that corresponded to Palaeozoic highs. These islands have subsequently been shown to have a diverse terrestrial reptile fauna which has latterly received much attention, (e.g. Robinson 1957, Whiteside 1984, Fraser and Walkden 1983).

The formation of "bone-beds" continued to fascinate geologists - Short (1904) for instance, envisaged that they were formed by vertebrates being stranded by great storms. He proposed that storms flooded low lying areas, and as the water receded the animals were trapped and died "en-masse". Wickes (1904) refined this model suggesting that the impersistent nature of the "bone-beds" was caused by the presence of "shifting shoals of fish" that lived in this "ephemeral lake". Llyod-Morgan and Reynolds (1908) on the other hand proposed that "bone-beds" were formed as a consequence of mass mortality as fish and reptiles swam into a hyper-saline lake. Richardson (1933) argued that they were synchronously deposited over the region and were formed by reworking and concentrating the bones present on earlier tidal flat deposits. The latter point he proposed because of the presence of *Ceratodus sp.* which he considered to be indicative of tidal conditions. Arkell (1933), in his seminal work on the Jurassic, did little to elaborate on Richardson's hyopothesis.

Kellaway and Oakley (1934) pointed out that as elements of the "Rhaetic" fauna (assuming normal marine conditions) were missing, notably:- crinoids, cephalopods, echinoids, corals and brachiopods and concluded that deposition was occuring in restricted marine conditions. Further they argued that reduced current activity caused black shale deposition and that the limestones formed in brief oxic events.

Johnson (1950) working on the faunal abundance of different bivalves (notably *Protocardia sp.* in the "Rhaetic" of south Nottinghamshire, recognised systematic variations in the fossil communities. To explain these he proposed undefined cyclic environmental processes. Elliot (1953) whilst discussing the "Westbury Beds" in Somerset, maintained that the fauna was stunted and

that some important marine groups were absent. He proposed that stunting in this context was caused by the "Swabian" nature of the facies. Bazley (1968) vigorously disputed this suggestion pointing out that there were no "normal forms" in the Westbury Formation by which dwarfism could be compared.

Kellaway and Oakley (1933) proposed that the driving force of the "Rhaetic transgression" was a eustatic sea level change. Hallam (1961) developed this theme - suggesting that eustatic sea level changes generally, were the controling factors behind alternating limestone and shale formation - with the shales being deposited in deep water, whilst the limestones were deposited in shallow water. Hamilton (1962, 1977) recognised a series of fining upward cycles in the "Westbury beds", to explain these he proposed that environmental cyclicicity was controling sedimentation. He suggested that initially high energy events, reworked the underlying sediment producing an erosion surface, which was immediately followed by deposition of a coarse (sandy or conglomeratic), carbonate rich lag, then, as a energy levels decreased the grain size fined upwards into mud. Hamilton also proposed, that the "basal bone-bed" was formed as a strand line lag, in the wake of the "Rhaetic transgression". The large clasts often contained within it, he suggested, were reworked from the still soft underlying marls. He concluded, in order to preserve the continuity of these soft clasts, that the transgression was of very low energy. By implication Hamilton infered that sea level changes were the driving force behind the energy fluctuations that caused the fining upward cycles.

Ivimey-Cook (1962, 1974), working on the Rhaetic in South Wales found that faunal variations were coupled with fining upward sediment cycles, thereby implying that changes in sedimentary regiemen were also effecting the organisms. He also suggested that despite the absence of ammonites in the British Rhaetic, the Westbury Beds were definately deposited in marine conditions. Their absence he ascribed to the fact that "they were generally scarce in the Rhaetian of Europe" - a point subsequently disputed by Reitner (pers. comm. 1986).

Bazley (1968) after examining one of Ivimey-Cook's (1962) cycles in detail aggreed that the Westbury Beds were deposited in marine conditions (on the basis that ophiuroids were present), that there were minimal salinity fluctuations and that water depths were mainly less than 30m. He found no geographical variations in the fauna and no evidence of faunal stunting. He also proposed that current activity had winnowed the shell debris concentrating it into discrete horizons.

Audley-Charles (1970) reviewed the Triassic palaeogeography and stratigraphy and placed the Rhaetian in the Upper Triassic, and noted that the main structural controls on sedimentation were the Worcester Graben and Bristol Channel Trough. He re-emphasised the "Swabian" nature of the facies and pointed to the stratigraphic significance of the "Rhaetian transgression".

Reif (1971 and 1976) discussed the Rhaetian and Muschelkalk "bone beds" in Germany and "bone bed" formation in general. He hypothesised that bones preserved in "bone-beds", may have had inorganic phosphate added to them, making them harder and thus more resistant to abbrasion. This process he called "prefossilization", and he considered it to have been significant during the formation of British Rhaetian "bone-beds".

Sykes (1977) specifically addressed himself to the formation of "Rhaetic bone-beds". He classified them according to the amount of reworking that the individual bone elements showed. Antia (1979), continued this reworking theme and suggested that no single model explained their formation, however he did suggest that they were formed in intertidal or subtidal environments. Duffin (1980) despite undetaking an extensive review of the Rhaetian vertebrate fauna did not attempt a detailed facies analysis.

Kelling and Moshriff (1977) measured the orientation of ripples and fossils in the Westbury Formation. They found that the prevailing current orientations were directed north-east/south-west, which they correlated

with the similarily trending Rhaetian shore line. They attributed minor discrepancies in the orientation directions to the variable shape of the organic components.

Jeans (1978) in a detailed clay analysis of the Upper Triassic recognised three major sedimentation cycles:-

1) Dunscombe megagroup.
2) Weston megagroup.
3) Bindon megagroup.

with the Westbury Beds being included in the latter. Each of these cycles has a hypersaline (Germanic facies) and marine (Alpine facies) depositional component. Jeans found that the Germanic facies had a characteristic detrital and neoformed clay assemblage, dominated by magnesium rich clays and dolomites. Whilst the Alpine facies only had a detrital clay component and was calcite rich. The Westbury Formation he proposed, after limited sampling, was deposited in Alpine facies conditions, whilst the underlying Blue Anchor Formation was deposited in hypersaline, Germanic conditions. Previous workers notably Reynolds (1947) and Hamilton (1977) had also considered the Blue Anchor Formation to have been formed in continental, hypersaline or "sabkha" conditions.

Mayall (1979) after a sedimentary analysis of the Rhaetian concluded that the Westbury Formation was initially deposited in a lagoon barrier complex, which he proposed deepened latterly into more open marine conditions. He suggested that the near shore facies were restricted and had reduced faunal diversity with respect to the fully marine offshore facies. He also noted that marine deposition was brought abruptly to a halt by tectonic uplift at the begining of the Lilstock Formation which caused the development of lagoonal environments.

Micropalaeontoloical aspects of the Rhaetian has been extensively researched by Anderson (1964), Orbell (1973), Fisher (1972) and Warrington (1976, 1977, 1978, 1980). Warrington and Fisher (in their various papers) found that the hypersaline facies were mainly unfossiliferous, but heralding marine conditions, they found a miospore assemblages in the top few metres of the Blue Anchor Formation, which was supplemented by organic walled microplankton at the onset of the Westbury Formation. Warrington (1980) found that floral diversity generally increased through the Westbury Formation, and then abruptly droped with the onset of lagoonal conditions in the Lilstock Formation.

Jones (1981) after geochemical and sedimentary analysis, proposed that the Rhaetian sea, after the initial transgression was brackish with a low diversity fauna; which later became marine with a higher diversity fauna. He proposed that energy cycles (possibly caused by storms or sea level variations) intermittently brought into the basin of deposition, coarse, arenaceous debris. He argued that the Westbury Formation contained both onshore and offsthore facies, and generally that it was deposited subtidaly in marine conditions. Jones also found significant fluctuations in the organic matter preserved in the shales, with a peak of 10% in the basal part of the upper shale sequence, he proposed that these fluctuations were a direct consequence of variations in phytoplankton productivity associated with changing water depths.

Hallam and Shaarawy (1982) compared the Rhaetian faunas of South Wales with those in Austria and concluded that the faunal diversity in Britain was reduced (in terms of species numbers), and that the forms present tended to be thin shelled compared with those in Austria. They suggested that this was due to decreased salinity in southern Britain.

Overall the current established view of Westbury Formation deposition in south west Britain was in: marine/brackish, restricted basins, which had bottom water anoxia and a restricted benthos. The anoxia was caused by high surface productivity in the Rhaetian Sea. The basins were believed to deepen slowly throughout deposition of the Westbury Formation, before abruptly shallowing at the beginning of the Lilstock Formation. Minor sea level variations caused fluctuating environmental energy levels which resulted in:- cyclic changes to the flora, fauna and sediment input. The absence of ammonites, was due to a geographical "accident" and the formation of "bone-beds" to a migrating strand-line associated with the "Rhaetian" transgression.

APPENDIX 2 Sample Localities.

Standard grid references of Westbury Formation outcrops examined in this study.

Name	Standard Grid Reference
Wainlode Cliff	SO846258
Westbury Garden Cliff	SO718128
Wetmoor Wood	ST741877
Aust Cliff	ST568899
Chipping Sodbury	ST725837
Carrefour	ST586814
Shepton Mallet	ST602429
St. Audrie's Bay	ST103432
Watchet Harbour	ST083435
Sedbury Cliff	ST559935
Penarth Cliff	ST186695
Lavernock Point	ST188682
St. Mary Wells Bay	ST176677
Burton Row	ST335516
Stowell Park	SP084118
Upton	SP231131

APPENDIX 3 Graphic Logs of each locality.

The logs have abbreviated symbols, which are explained below:-


Limestone.


Shale.


Dolomite.


Detrital sand.


Bivalves.


Way up indicator for shelly debris.


Gastropods.


Phosphatic debris.


Echinoderm debris.


Algal fabrics.


Bioturbation.


Wave ripple lamination.


Coated grains.


Cobble grade clasts.

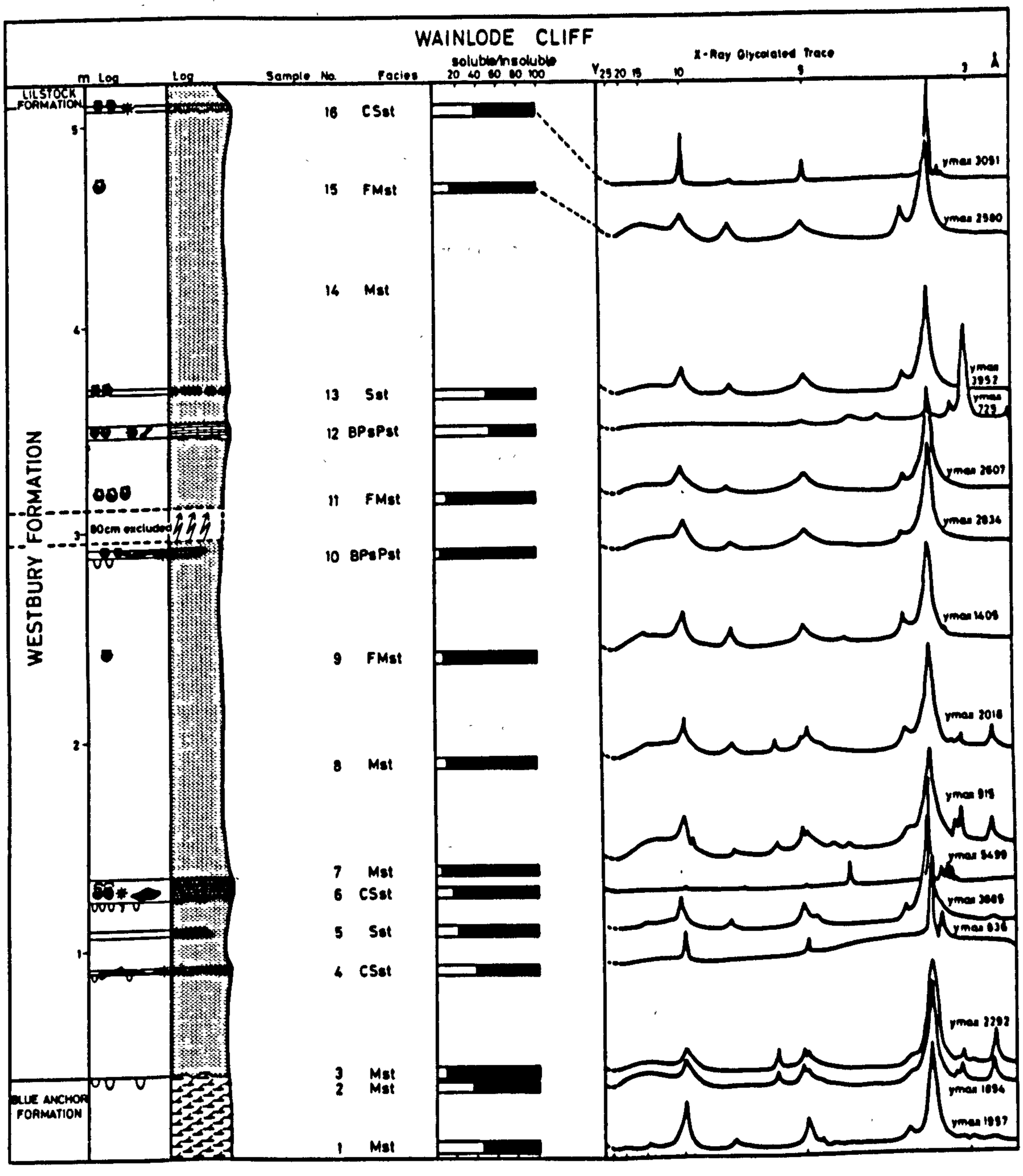

Authigenic pyrite.


Fibrous calcite fabrics.

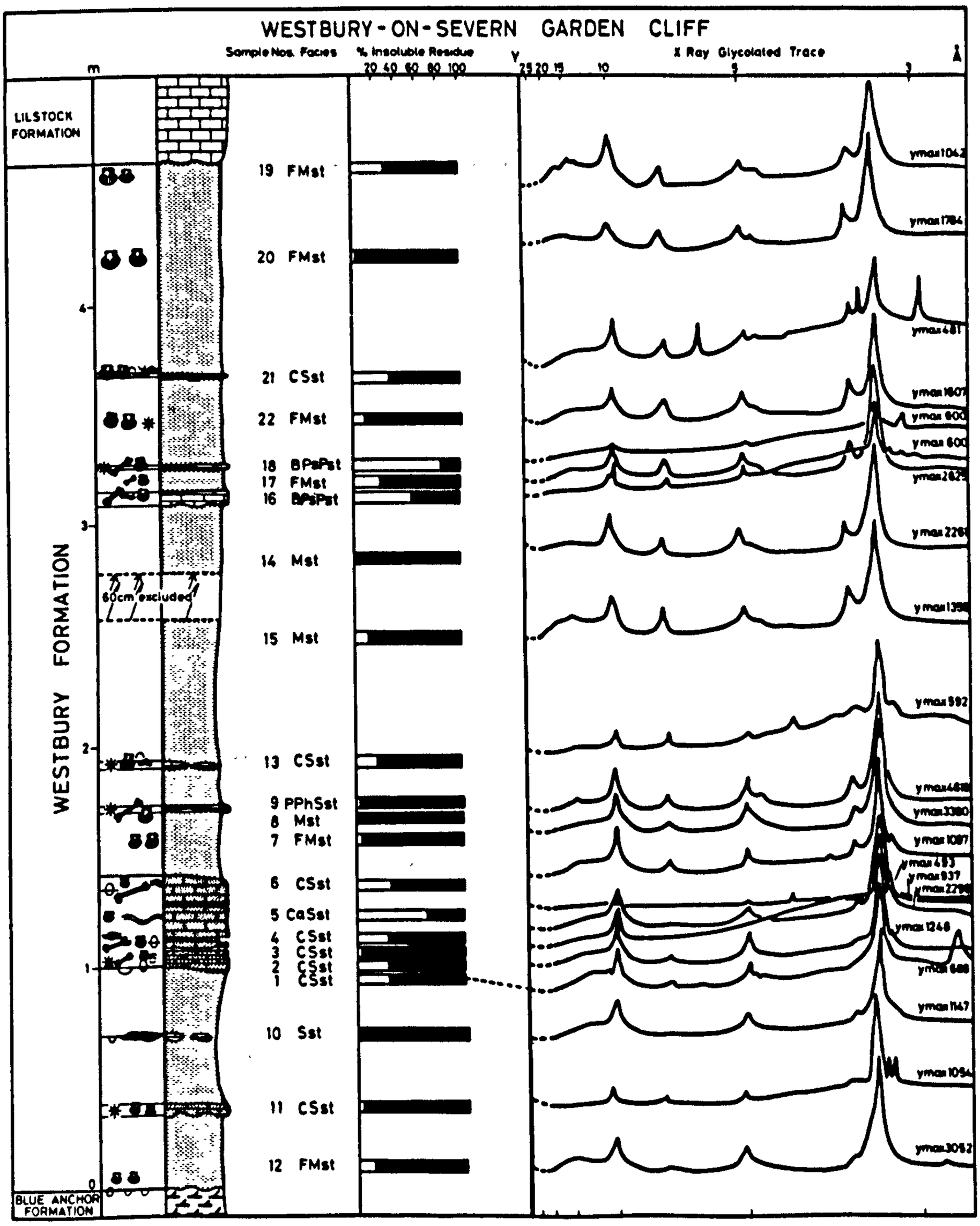

Section excluded from log.

The peak height of all the logs is normalized to 100% to make mineral comparison easier.

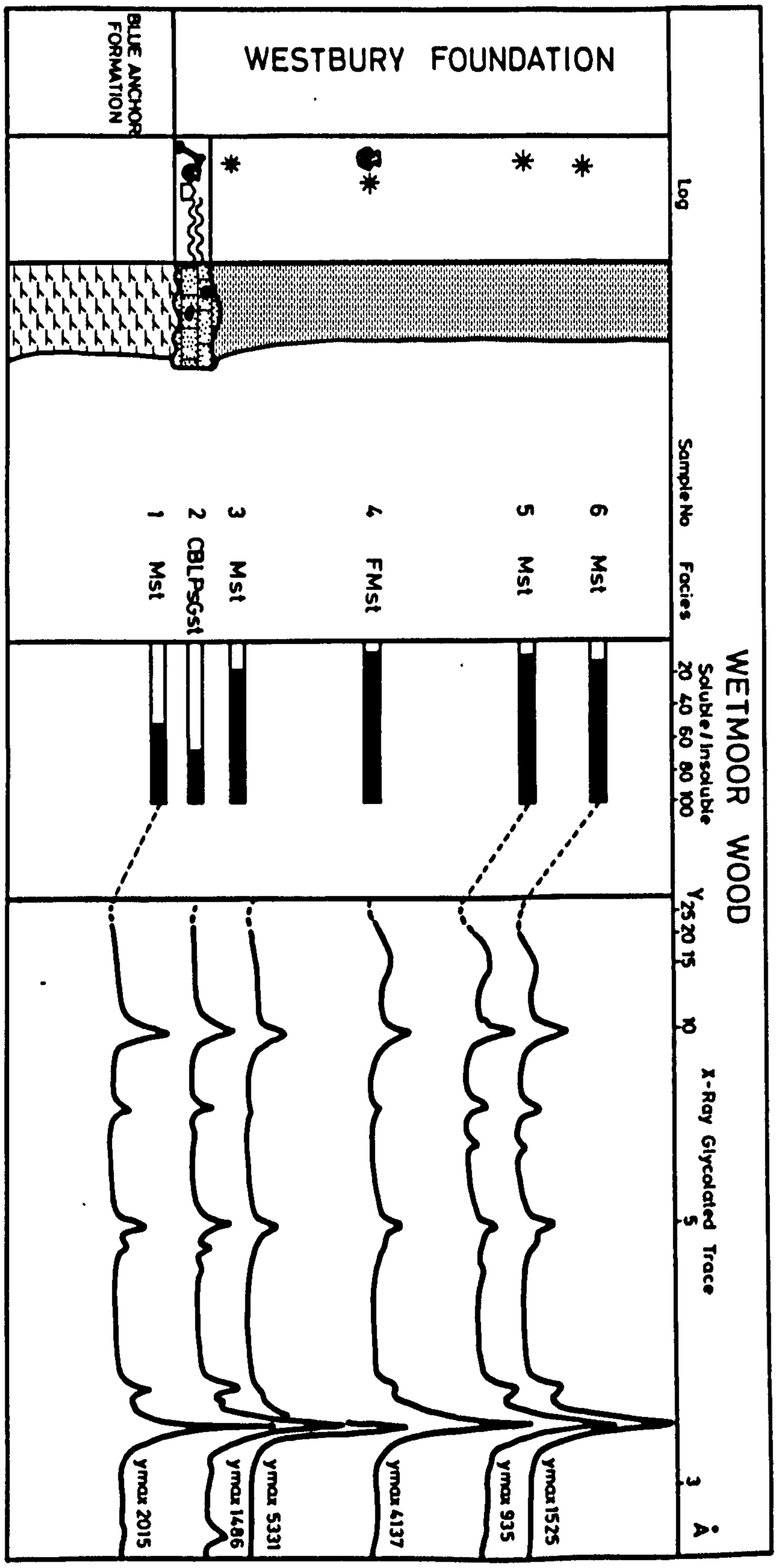
Log from Wainlode Cliff (SO846258).



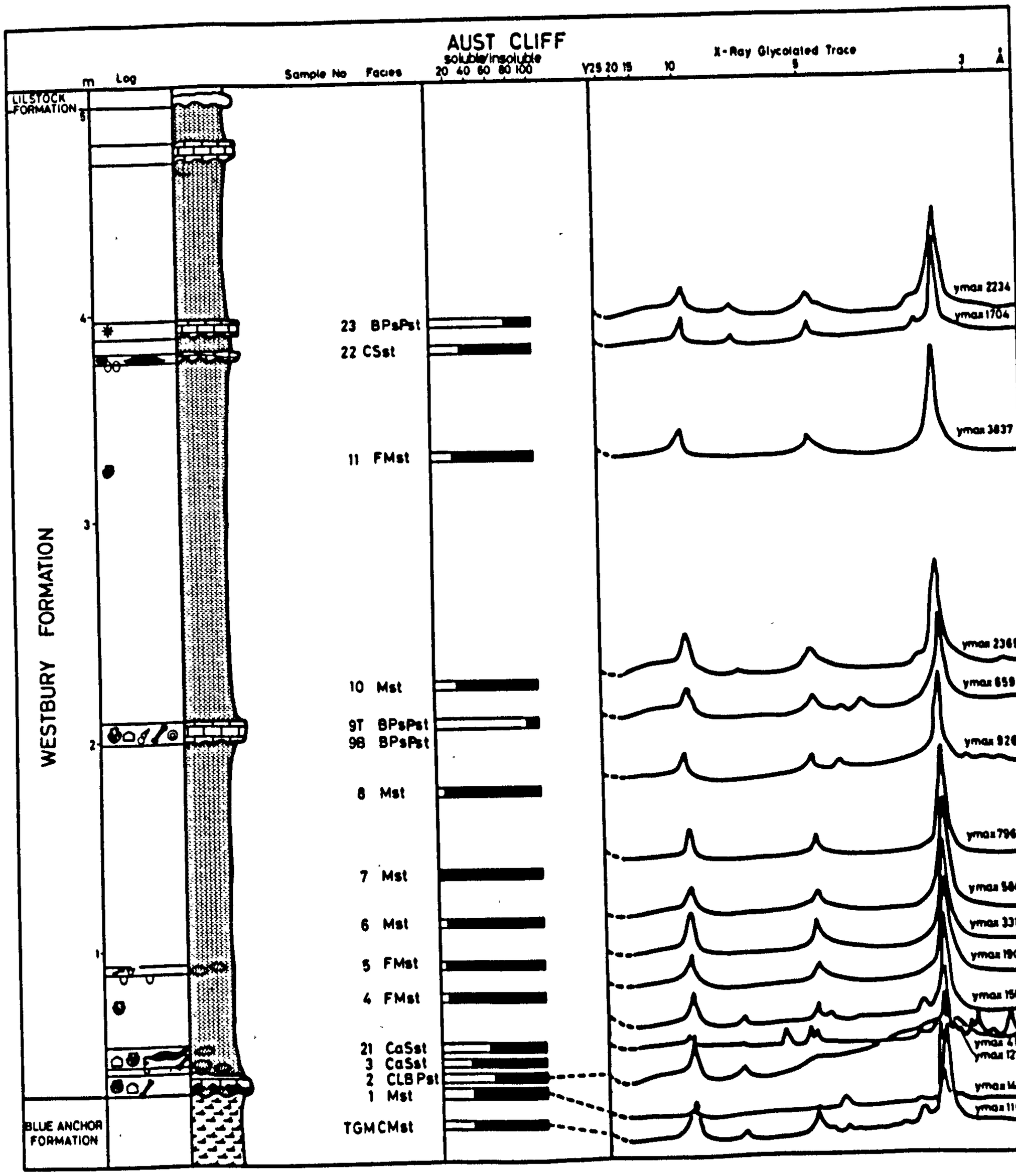
Log from Westbury Garden Cliff (SO718128).



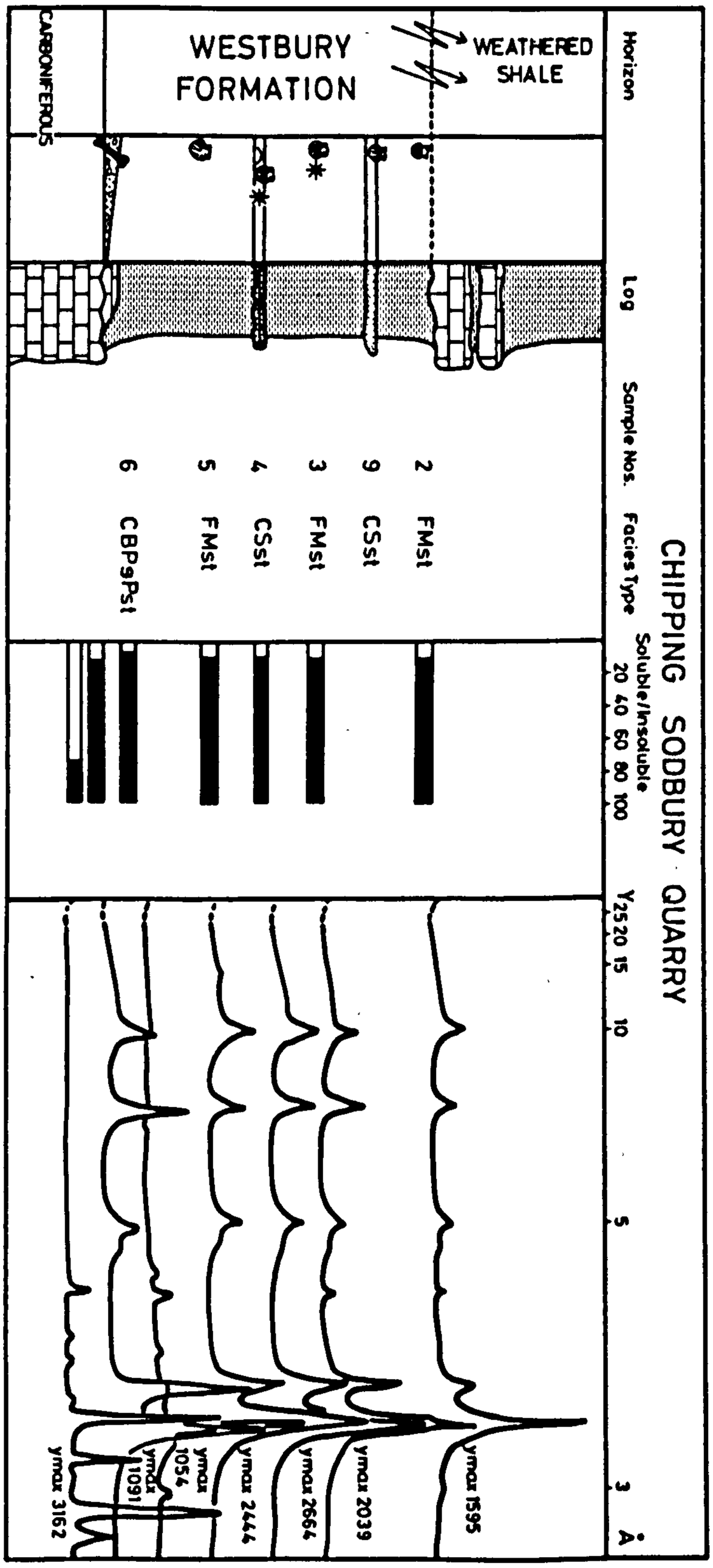
Log from Wetmoor Wood (ST741877).



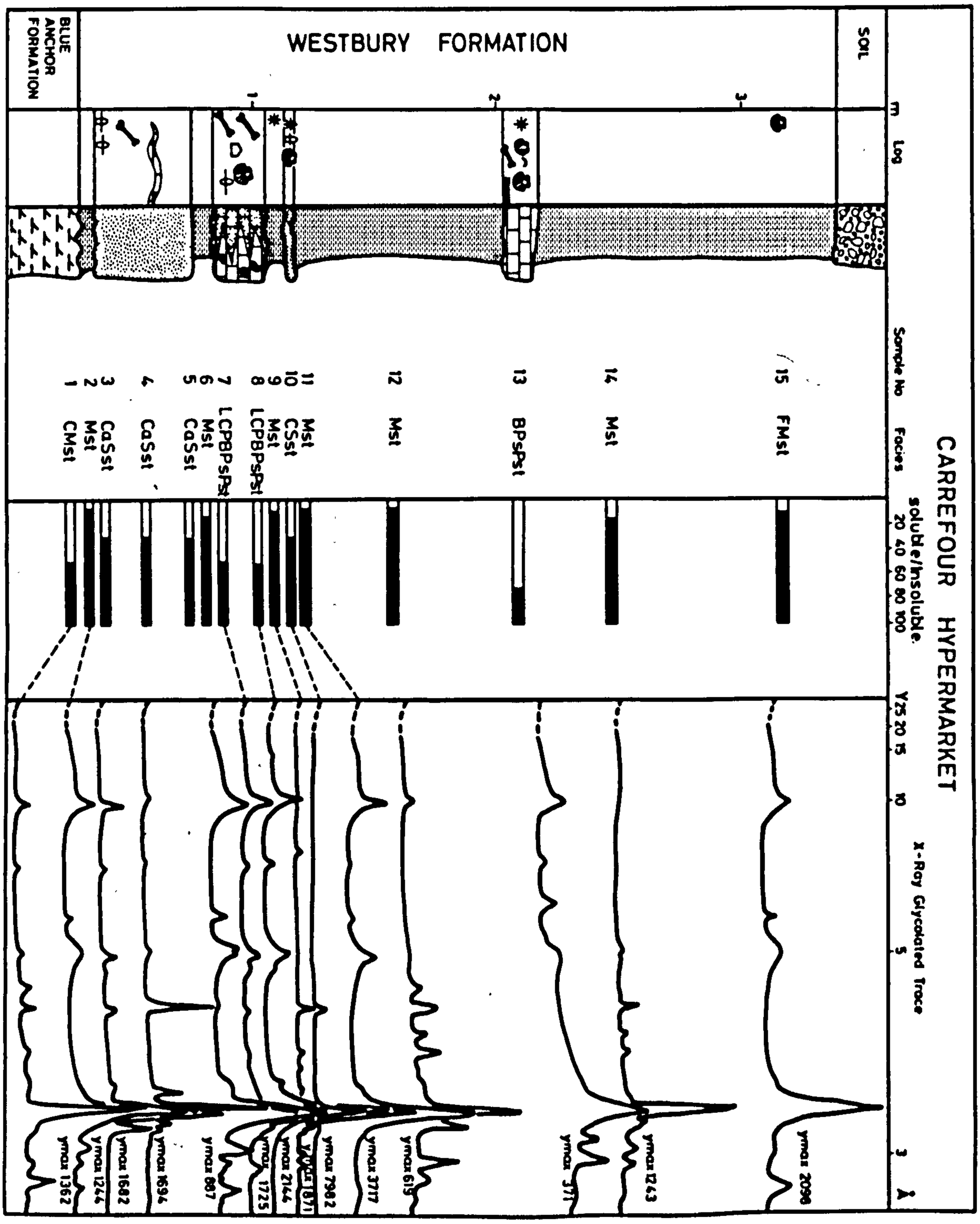
Log from Aust Cliff (ST568899).



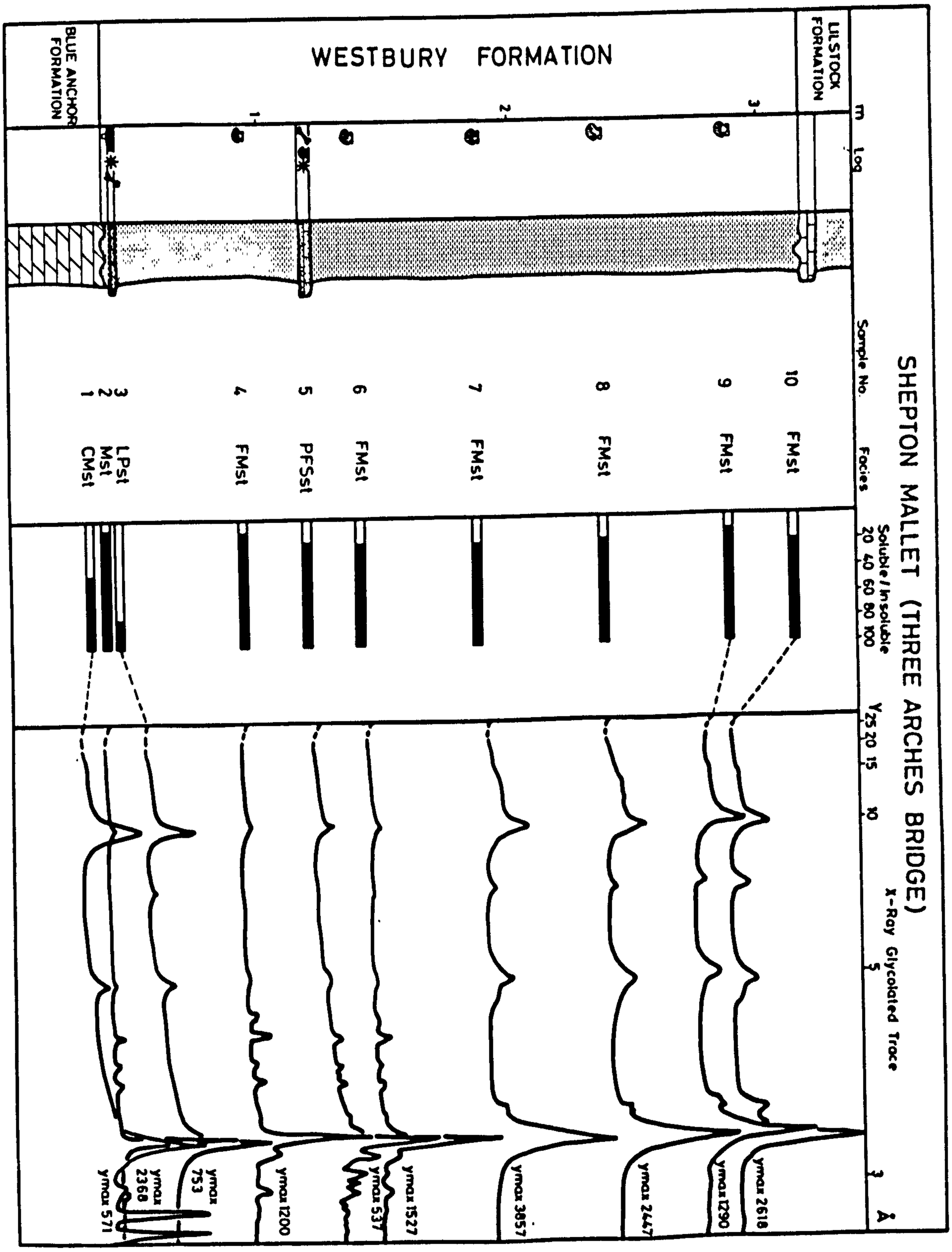
Log from Chipping Sodbury (ST725837).



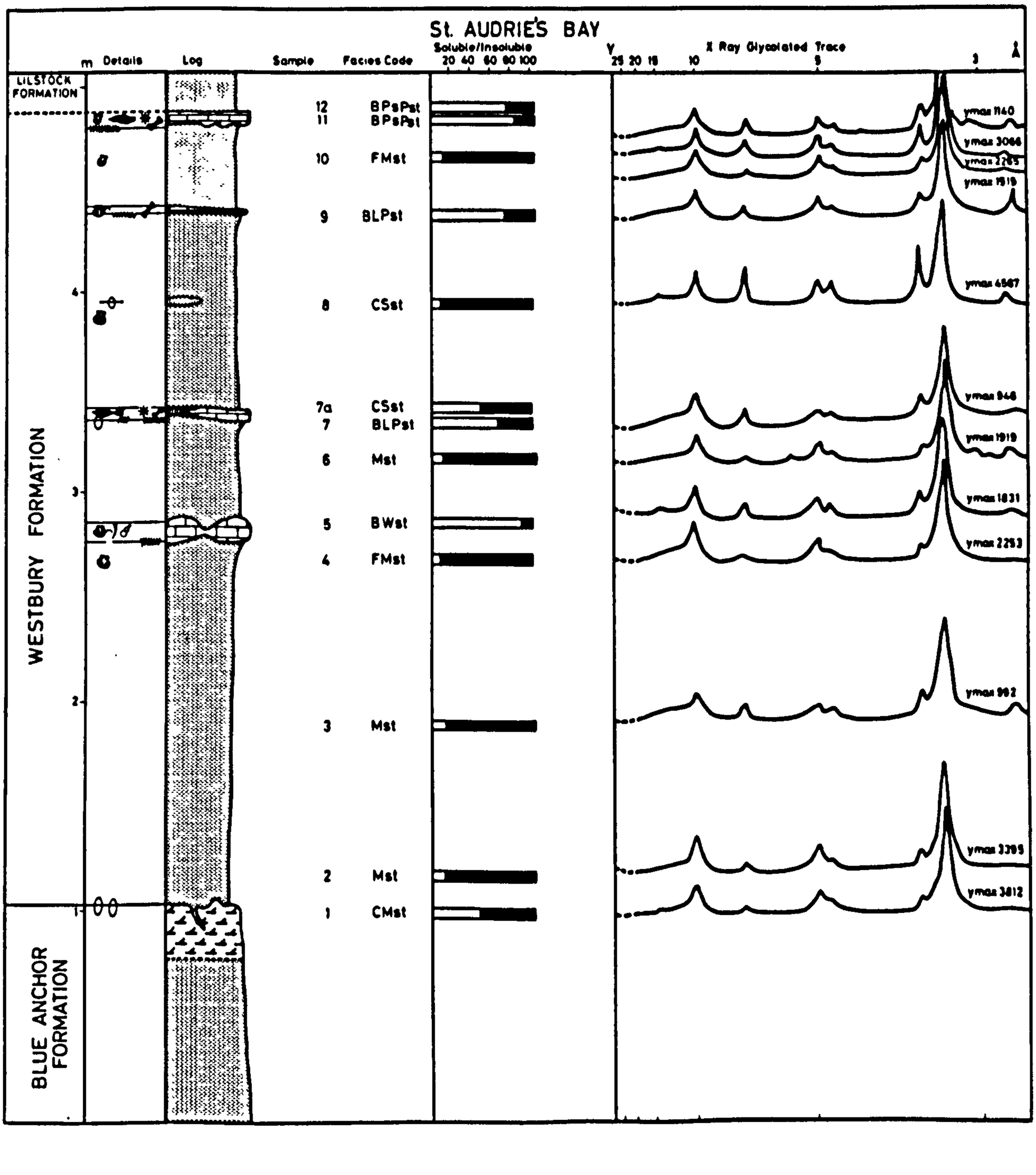
Log from Carrefour (ST586814).



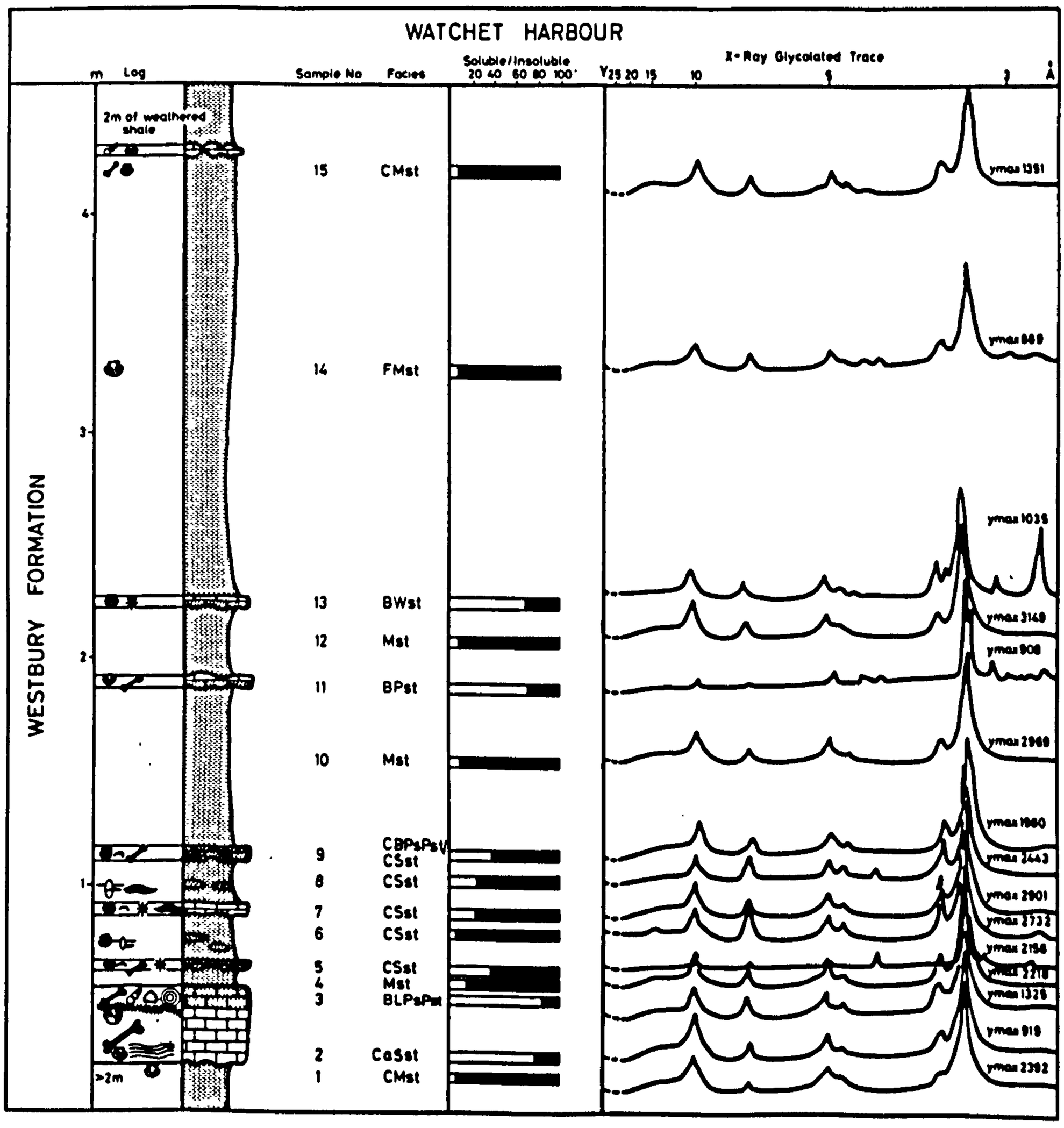
Log from Shepton Mallet (ST602429).



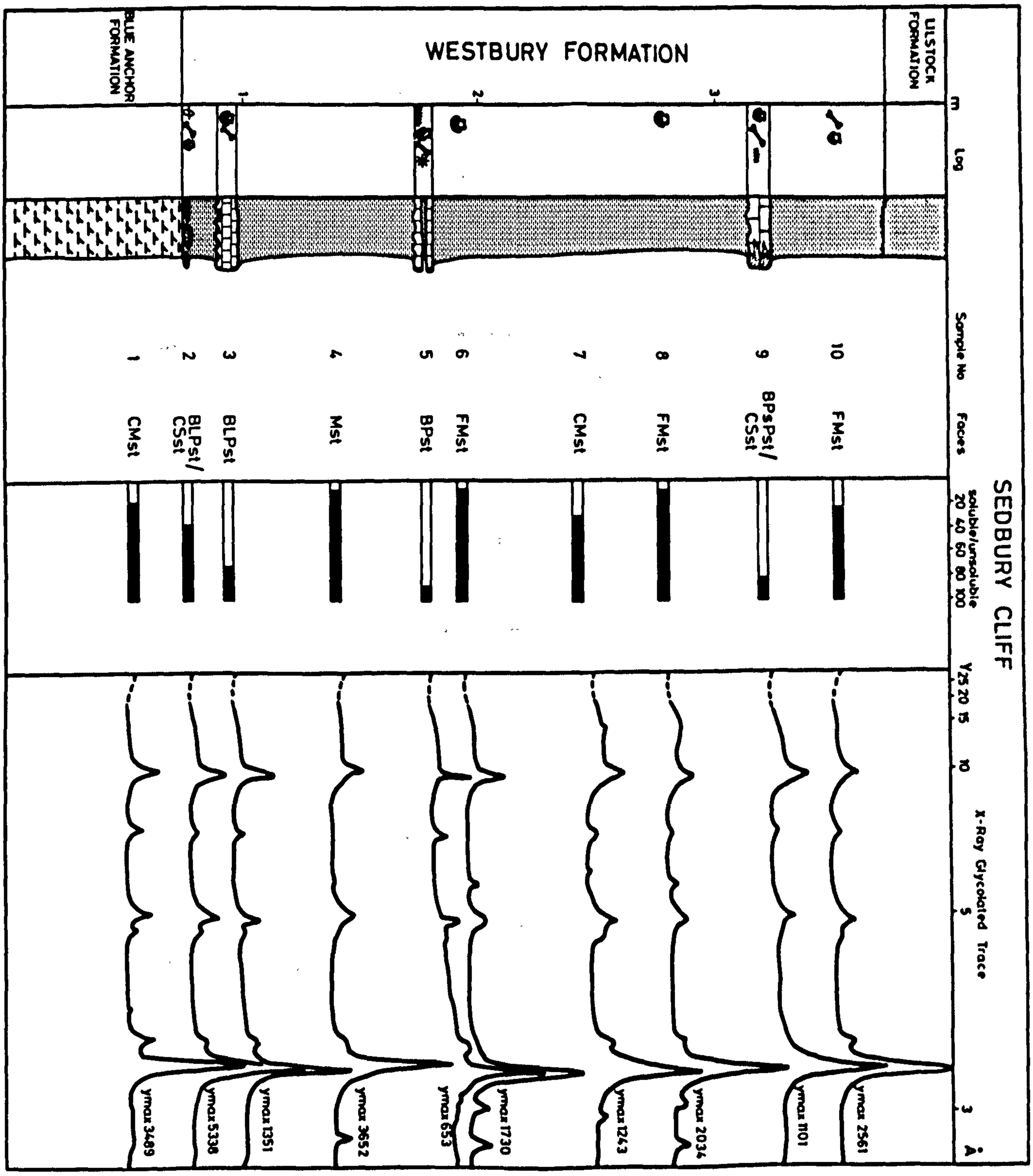
Log from St. Audrie's Bay (ST103432).



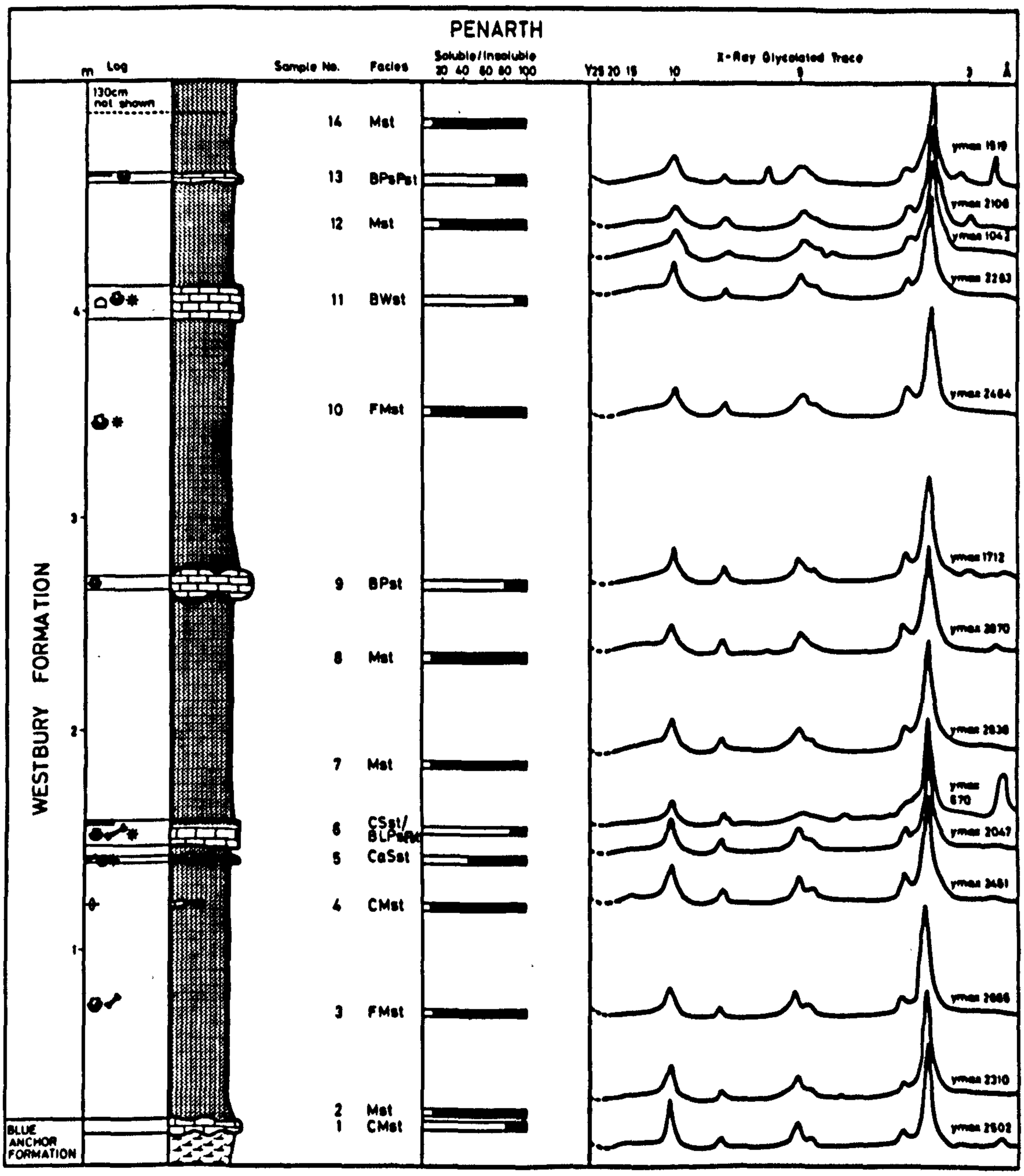
Log from Watchet Harbour (ST083435).



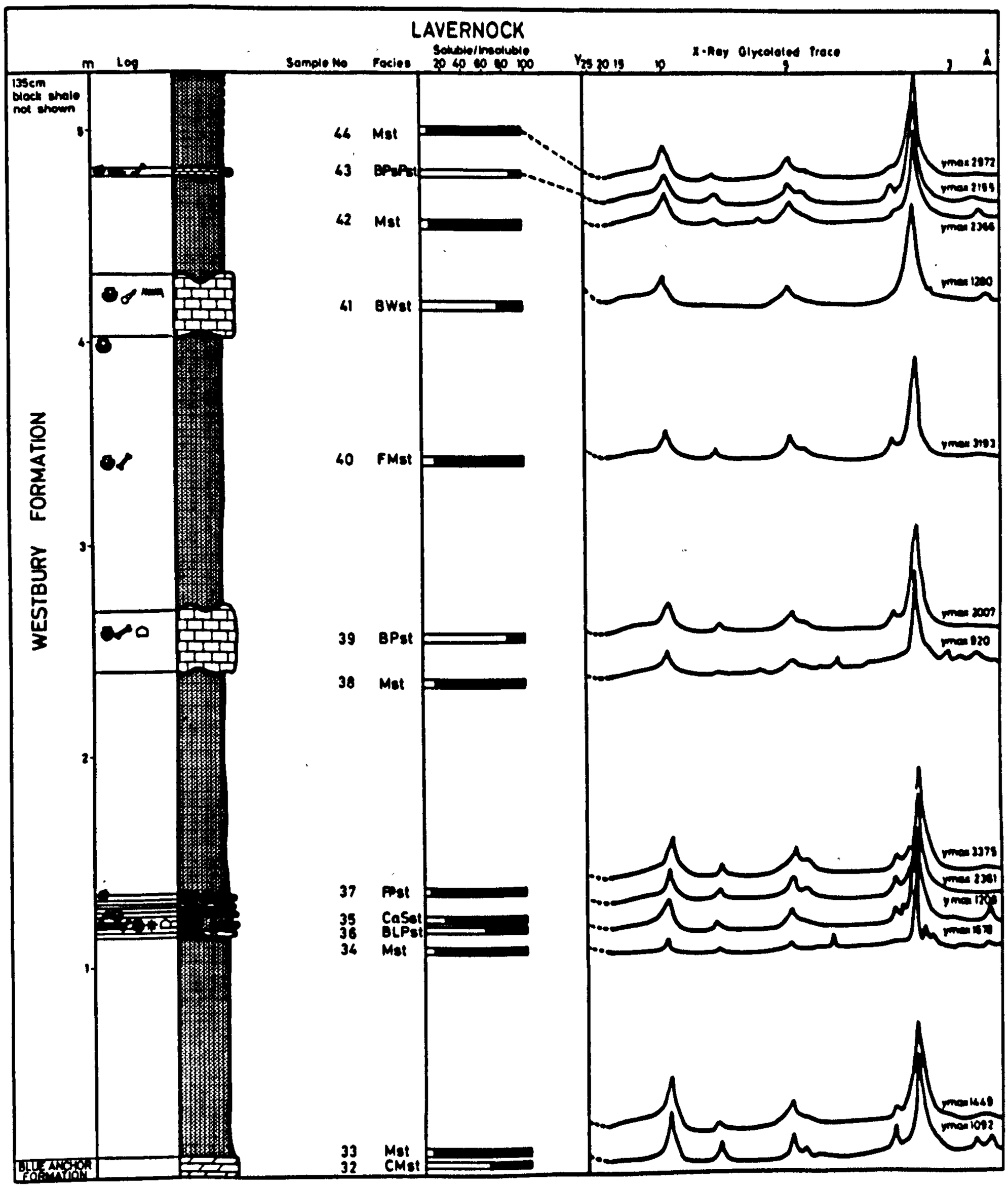
Log from Sedbury Cliff (ST559935).



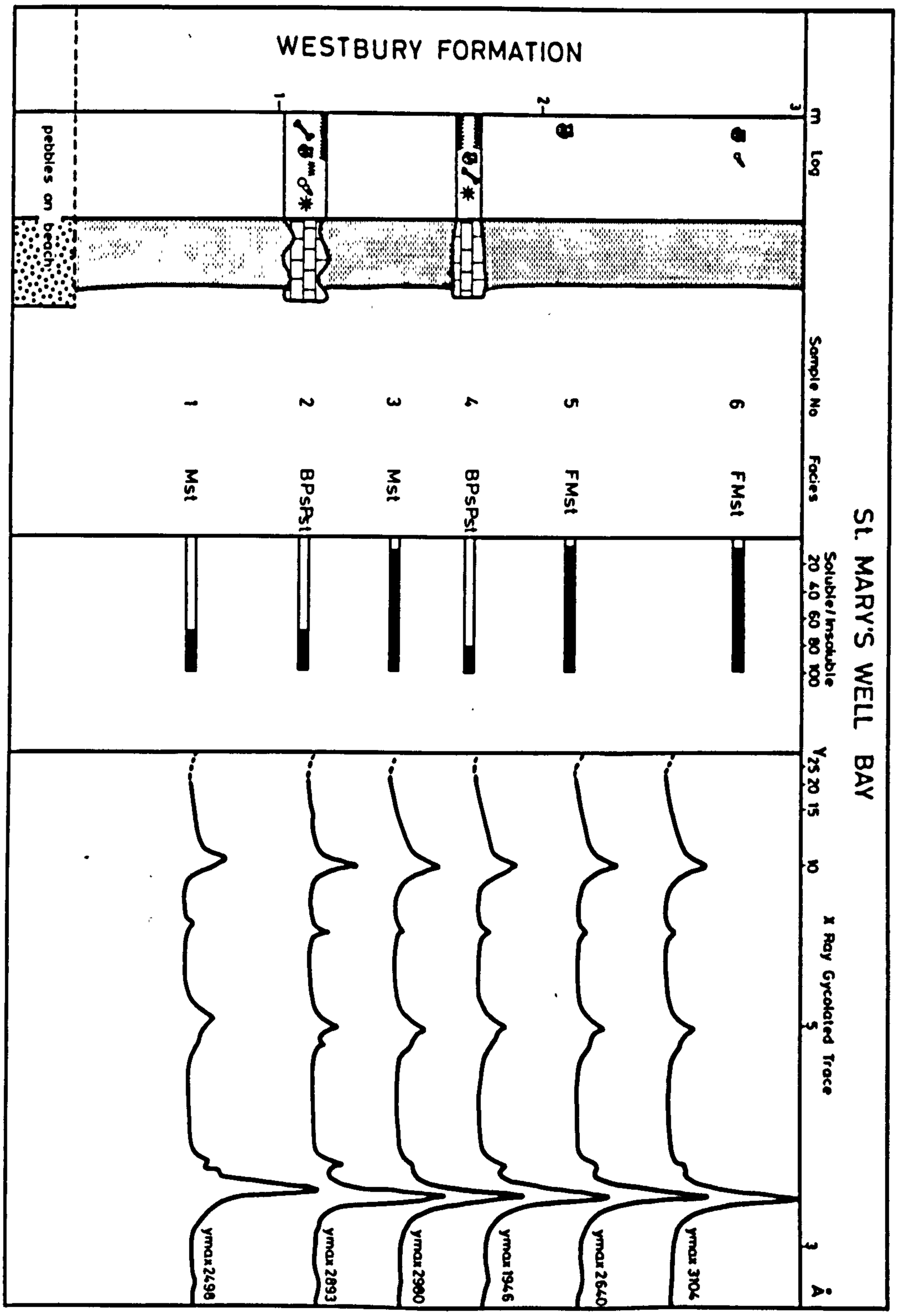
Log from Penarth Cliff (ST186695).



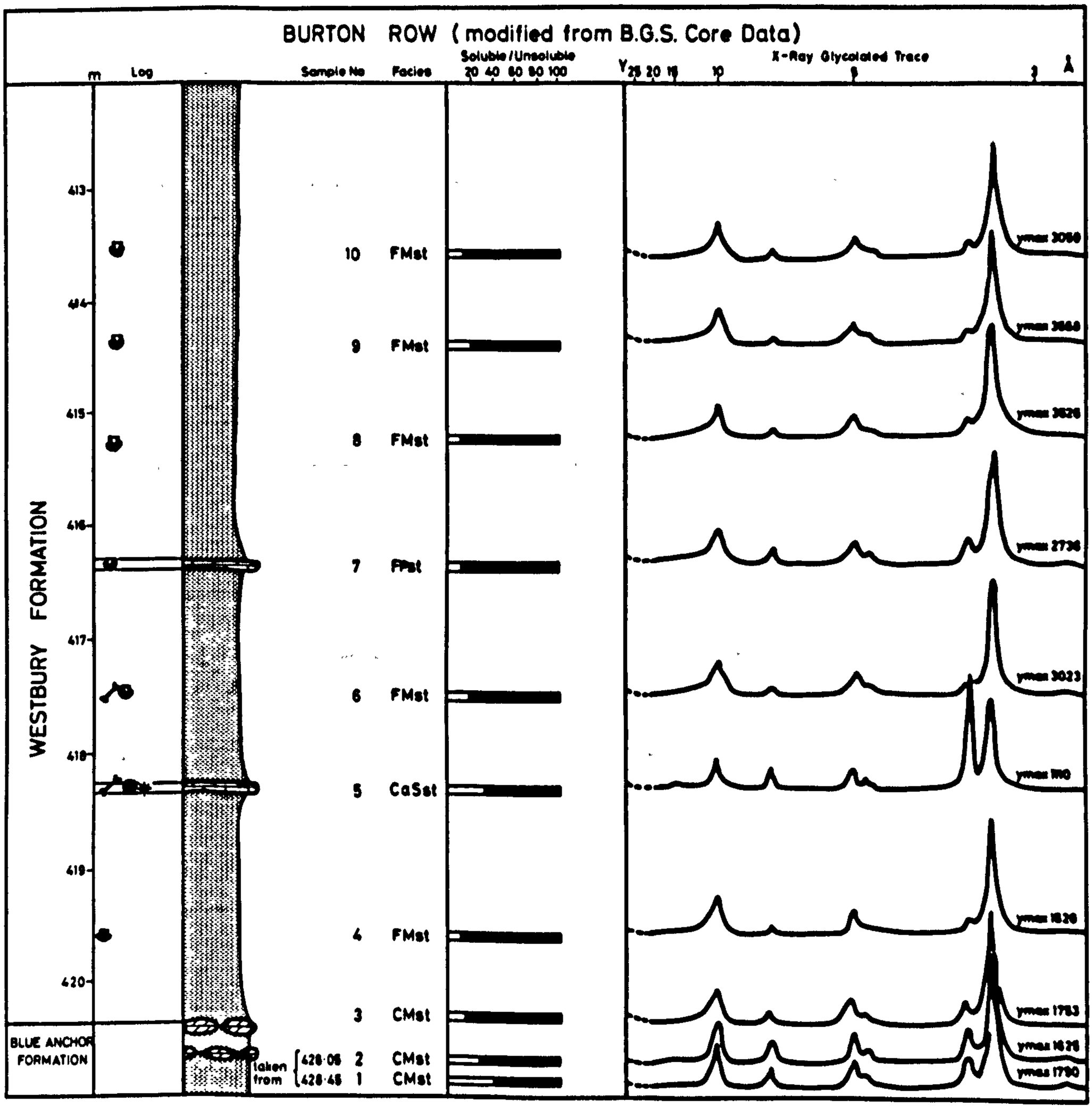
Log from Lavernock Point (ST188682).



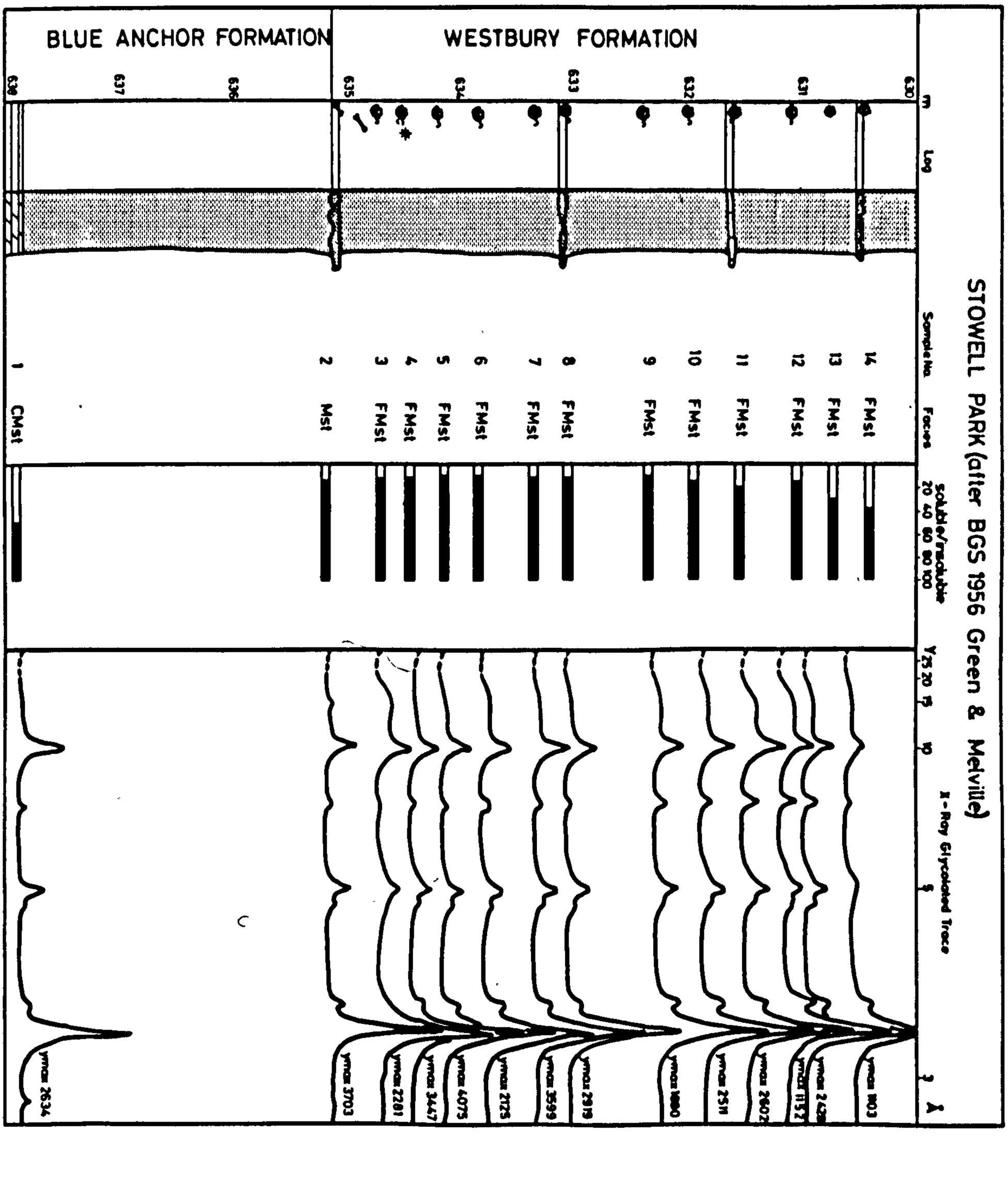
Log from St. Mary Wells Bay (ST176677).



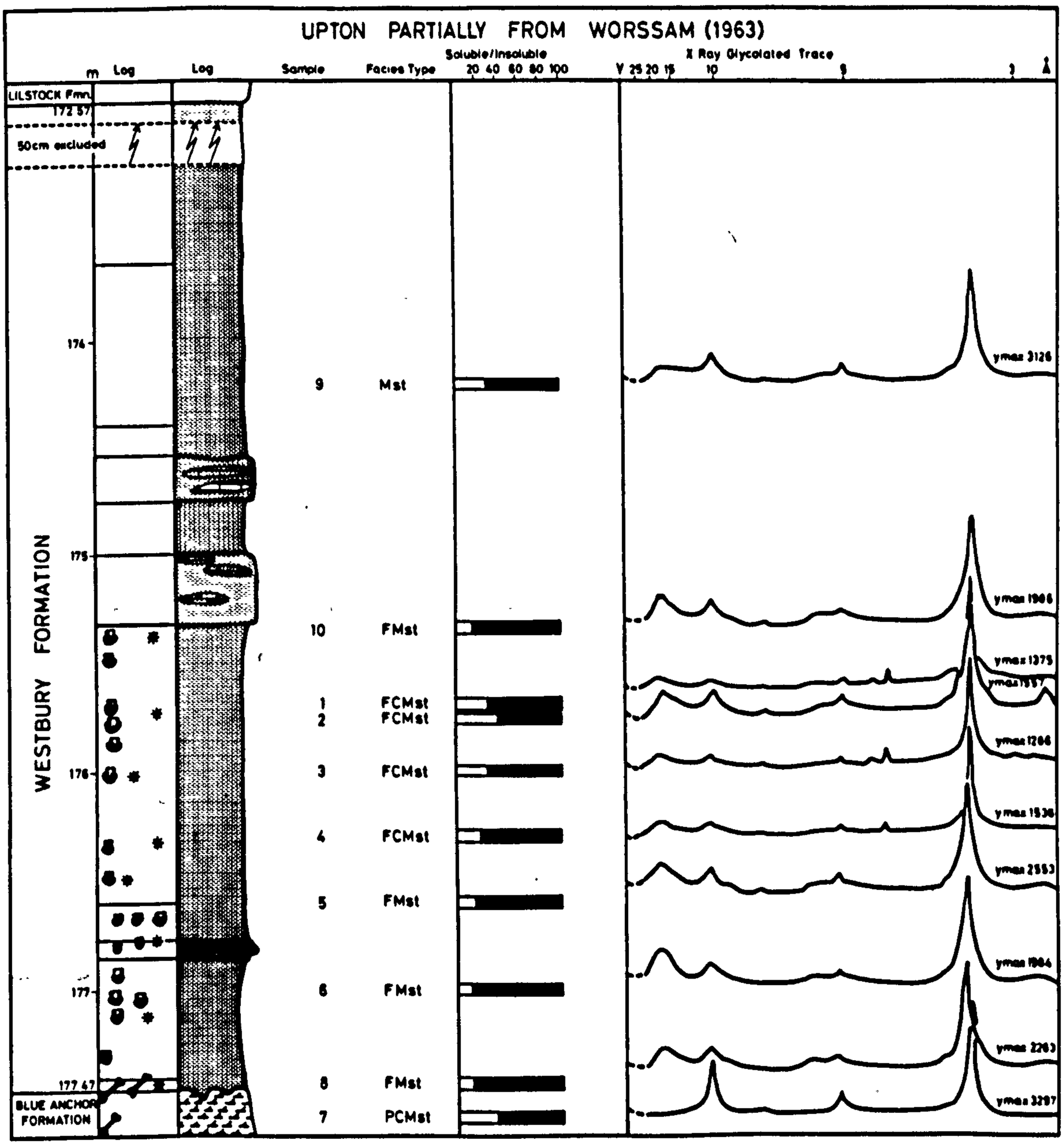
Log from Burton Row (ST335516).



Log from Stowell Park (SP084118).



Log from Upton (SP231131).



APPENDIX 4 Faunal Analysis and palaeoenvironmental discussion.

A detailed faunal analysis was not a specific objective of this project (for such information see Ivimey-Cook 1962, Bazley 1968 and Mayall 1979). However many organisms were collected and their taxonomy is reviewed (after Owen (1839), Moore (1861), Vaughan (1904), Richardson and Tutcher (1914), Von Huene (1933), Reynolds (1947), Cox (1962), Cox (1963), Savage and Large (1966), Moore *et al.* (1969), Erickson (1972), Duffin (1980), Martin (1980) and Martin (1981)) in the following sections, with additional comments on their palaeobiology (after Stanley (1970) and Schafer (1972)) and shell mineralogy (after Taylor *et al.* 1973):

(1) Bivalvia.

The bivalve fauna in the Westbury Formation is relatively diverse, with 9 genera described. Unfortunately the species status of the genera is unsure.

i) MYTILOIDEA.

MYTILIDAE.

Modiolus sp.

The animal was byssate, probably lived semi-buried and may have been able to tolerate salinity fluctuations (after Hudson 1963). Its shell was composed of aragonite (assuming warm water water) and its structure was nacreous (after Taylor *et al.* 1973).

ii) PTERIACEA.

PTERIIDAE.

Rhaetavicula sp.

A byssate animal that cemented itself by its right valve to the substrate. It had a characteristic assymmetrical auricle, which Cox (1962) argued would enhance inhalent and exhalent current separation. Stanley (1970) noted that examples from the modern Pterioida with well developed wings often attach themselves to soft corals (eg. Alcyonarians). The shell of *Rhaetavicula* was composed of both calcite and aragonite, and its structure both nacreous and prismatic (after Taylor *et al.* 1973).

iii) PECTINACEA.

PECTINIDAE.

Pecten sp.

The animal was probably byssally attached (Stanley 1970). Its mineralogy was both calcitic and aragonitic, and its shell structure is both cross-lamellar and foliated (after Taylor *et al.* 1973).

iv) TRIGONIACEA.

MYOPHORIIDAE.

Lyriomyophoria sp.

A burrowing animal that probably lived in a soft substrate (after Stanley 1970). Its shell was composed of aragonite and its structure both prismatic and nacreous (Taylor *et al.* 1973).

v) CARDITACEA.

PERMORPORIDAE.

Permorphorus sp.

Stanley (1970) whilst commenting on the Carditacea as a whole noted that: "divergence of both the Arcidacea and Carditacea into byssally attached and free burrowing groups has produced adaptive convergence of the two families. The compact species are free burrowers; whilst the elongate species (e.g. *Permorphorus sp.*) (are epifaunal) and were attached by a strong byssus". *Permorphorus sp.* had an aragonitic shell, whose structure was cross-lamellar (after Taylor *et al.* 1973).

vi) CARDITACEA.

CARDITIDAE.

Palaeocardita sp.

Palaeocardita sp. was probably a free shallow burrower, (see comments by Stanley (1970) above which were applied to *Permorphorus sp.*). Its shell was composed of aragonite and it had a cross-lamellar texture (after Taylor *et al.* 1973).

vii) CARDIACEA.

CARDITIDAE.

Protocardia sp.

Protocardia sp. was a burrowing bivalve that used its ribs to aid traction whilst digging in the sediment (after Stanley 1970). It had an aragonitic shell composed of cross-lamellar fibres (Taylor *et al.* 1973).

iix) CYPRINACEA.

ARCTICIDAE.

Isocyprina sp.

A shallow burrowing bivalve which probably lived in soft, muddy substrates. Its lifestyle may have been analogous to the extant *Mulinia sp.* which "inhabits soft muddy bottoms of restricted bays and lagoons" Stanley (1970). Its shell was composed of aragonite and consisted of cross-lamellar fibres (Taylor *et al.* 1973)

ix) PHOLADOMYACEA.

CERATOMYEIDAE.

Pteromya sp.

Pteromya was probably a burrowing bivalve (Stanley 1970). Its shell was composed of aragonitic and its shell structure was both nacreous and prismatic (Taylor *et al.* 1973).

(2) **Gastropoda.**

Gastropods in the Westbury Formation are generally rare, with the exception of some horizons at Lavernock Point (Ivimey-Cook 1962). Two genera have been recognised:- a low spired "Naticid" form, and a high spired form. The high spired form is present in sections in south Wales and north Somerset. The gastropods have been briefly described by Ivimey-Cook (1962), Bazley (1968) and Mayall (1979), however their detailed taxonomy is unknown. Generally the gastropods are assumed to have been detrital feeders, but in this context there is no evidence that they are preserved *in-situ*, so this observation is in part irrelevant.

(3) Ophiuroidea.

Complete examples of brittle stars are very rare although they have been mentioned by Reynolds (1947) and Bazley (1968) as being present in the shales at Aust Cliff and in South Wales. During the course of this study, ophiuroid limbs were observed in some of the carbonate units, notably in Aust 9. Disarticulated echinoderm plates are occasionally encountered in thin section.

The ophiuroids are ascribed to:- *Ophiolepis damesi.* Palaeoenvironmentally, echinoderms (including Ophiuroids) are generally considered to be stenohaline. There is good evidence however, that some extant forms, notably *Asterias rubens* will tolerate brackish water (Schafer 1972). The Westbury Formation organic rich muds were mainly deposited during anoxidic, sulphidic conditions. At face value this would stop echinoderms from colonizing the sediment. Ophiuroid presence in the muds is therefore a problem. However, on the basis that most echinoderm material is composed of disarticulated debris, it is assumed that it was transported into the basin by the storm events. Clearly the odd living animal would also be transported into the basin, by the "event" and thus would remain articulated. Its death and subsequent preservation would follow, either as a consequence of the re-establishment of anoxia, or, as a consequence of being buried.

(4) Crustacea.

Rare Crustacean remains are present in the Westbury Formation assosciated with coprolites (Duffin 1978) which are ascribed to: the Decapod *Tropifer laevis* (after the earlier work of Gould (1857), Oppel (1858) and Stoddart (1876)). The animal are not preserved *in-situ.*

Mayall (1979) suggested that some of the abundant burrow systems notably *Thallasanoides sp.* that are preserved in the carbonate facies may have been formed by decapods. Decapods despite their relative scarcity as body fossils may have been a significant part of the fauna during oxic conditions.

The ostracod fauna from the Rhaetian has been carefully reviewed by Anderson (1964). Very few examples were found during the course of this study, with the exception of one horizon at Aust (Aust 9), unfortunately the taxonomy of these specimens is unknown.

(5) **Calcareous Algae.**

Poorly developed laminite fabrics, coated grains, micritized allochems and clotted grains may be attributable either dirctly to algal remains or indirectly to their presence and "activity in the sediment". Unfortunately the microstructure of these algae is not preserved, due to the development of neomorphic fabrics thus their detailed taxonomy is unknown. In the following subsections these textures will be discussed:-

(a) **Clotted grains** are present beneath some of the disarticulated bivalves, as these structures do not cross cut the shell material they are considered to be detrital rather than neomoprphic products and probably have an algal or fungal origin (Fabricius 1977, Marshall pers. comm. 1985). These "clotted grains" are interpreted as being spherulites.

The presence of **micrite envelopes** surrounding bivalve debris is indicative of either endolithic boring algal or fungal activity (Bathurst 1975, Kobluk and Risk 1977 and Golubic *et al.* 1975). The following endolithic algal groups are known: coccoid cyanophytes, chlorophytes and rhodophytes (Kobluk and Risk 1977).

Where it it possible to establish that the micrite envelopes have an algal rather than fungal origin they can be used as palaeo-depth indicators as the algae are restricted to the photic zone, whereas the fungi are known from depths down to 871 m. (Hook *et al.* 1984) and from within the sediment (May and Perkins 1979). Bathurst (1975) suggested that algal borings can be distinguished from fungal borings on the basis of size, with

the former being about 6 microns in diameter and the latter are only 2 microns in diameter. On this criteria the micrite envelopes in the Westbury Formation were produced by algae, which indicates deposition in the photic zone.

(c) **Coated grains** (or cortoids) have also been observed in the carbonate units in the Westbury Formation. They usually manifest themselves as bright luminescing, non-ferroan calcite grain coats, that surround bioclastic fragments Their formation is a contentious issue (Bathurst 1975, Brand and Veizer 1983) however it is known that they normally form in marine conditions, probably as the result of the interaction of organic compounds and calcium carbonate. Whether or not they are formed by the direct influence of organisms is not known. However if direct biological precipitation is causing their formation it is probably limited to the effects of Codiacean algae (Loreau 1984) and cyanophytic bacteria (Riding 1983).

In conclusion it is likely that algae and cyanophytic bacteria were present during oxic deposition. It is therefore most probable that Westbury Formation deposition occurred in the photic zone.

The origin of micrite.

Calcareous muds in the Westbury Formation are generally characterized by having a bright luminescence and being composed of non-ferroan calcite. Unfortunately much of the micrite has been recrystallized, and thus many of its diagnostic, genetic features have been destroyed. Micrite formation generally, has been reviewed by Bathurst (1975) and Flugel (1982). So only a cursory review is presented here.

A number of sources are known to have contributed to the supply of the calcareous mud in this study. Notably the debris produced by boring sponges and endolithic algae and the material produced by the abbrasion and disintegration of calcareous allochems. There is circumstantial evidence that

anoxic cyanophytes may have been present. Krumbein (1974) has shown that they precipitate micrite onto their sheaths, and so their decomposition would supply calcareous mud. A number of physiochemical and biochemical models of lime mud production may also be significant. Maurin and Noel (1977) argued that the decomposition of bacterial amino acids and the production of ammonia, would raise the local pH sufficiently to produce micrites. Berner (1969) argued that the decay of macro-organisms would have a similar effect.

The influence of diurnal changes in algal metabolism may also significantly change the redox potentials of sea water, particularly in enclosed basins (Friedman and Forer 1982). Algal metabolism causes the pH to increase during the day, and decrease at night, due to the changing light/dark metabolism of the algae. Friedman and Forer (1982) argued that this might be sufficient to cause micrite production.

Clearly the Westbury Formation micrites have many potential sources. It is almost certain that some of the mud was derived from the destruction (both physical and biological) of other allochems, but it may also be derived from the decomposition of bacteria and the associated effects of pH changes during the oxidation of organic matter. Potentially there is a very interesting relationship between the organic matter and the micrites. It is not known if purely physiochemical effects were influencing lime mud production.

APPENDIX 5 Vertebrate Taxonomy and palaeoenvironmental conclusions.

Duffin (1980) discussed in detail the taxonomy of the fish and sharks from the Westbury Formation. It is therefore not intended in this study, to go into any detail about these groups. Instead Duffin's work will be briefly summarized.

Sharks

Palaeospinacid sharks.

Palaeospinax sp.

Nemacanthus sp.

Hybodont sharks.

Polyacrodus sp.

Hybodus sp.

Lissodus sp.

Acrodus sp.

Pseudodalatias sp.

Bony fish.

Actinopterygii.

Holostei.

Semionotidae.

Sargodon sp .

Lepidotidae.

Lepidotes sp.

Chondrostei.

Birgeriidae.

Birgeria sp.

Palaeoniscidae.

Gyrolepis sp.

Colobodontidae.

Colobodus sp.

Duffin (1980) proposed that the sharks were stenohaline, and their presence indicated marine depositional conditions. However the palaeoecological implications of finding sharks are not straight forward as most modern sharks can tolerate brackish water at least temporarily, and one species tolerates freshwater (living in Lake Nicaragua Schafer 1972). Despite this however Sharks are considered to be definitive palaeoenvironmental indicators.

Common small conical teeth from the Westbury Formation have been the subject of considerable taxonomic speculation. Reynolds (1947) suggested that they were derived from labyrinthodont amphibians. With this in mind he suggested that the Westbury Formation was deposited in a fresh/brackish water lagoon. Savage and Large (1966), after re-examining the teeth and new mandibular material, concluded instead, that they were derived from *Birgeria sp.*, thus negating Reynolds's (1947) palaeoenvironmental conclusions. Duffin (1981) reopened the debate and re-ascribed the conical teeth, and some mandibular symphysial remains, to plagiosaur amphibians. Further examination of the material in this study, and by A. Milner pers. comm. (1982), suggests that Duffin and Reynolds's material, was most likely to be derived from *Birgeria sp.* and therefore does not impart any particular environmental significance.

Dipnoi.

Lungfish remains, in particular tooth plates are common at certain localities in the Westbury Formation (notably Aust). The taxonomy of Triassic lungfish has been reviewed by Martin (1980 and 1981) and he showed that the multitude of forms that had previously been erected on size variations, were in fact the same species. Detailed taxonomic analysis on these Rhaetian lungfish has not been attempted, because apart from tooth plates, other remains are rare. Thus the Westbury formation forms are only given generic status:-

Ceratodus sp.

Reynolds (1947), suggested, using the habitat preferences of the extant *Neoceratodus sp.* as a living analogue, that the presence of *Ceratodus sp.* in the Westbury Formation was indicative of deposition in marginal or ephemeral conditions. Lung-fish remains in the Triassic are however known associated with ammonites in the Alps (Martin pers. comm. 1980) thus since the Triassic they must have undergone niche contraction and thus are unreliable palaeoenvironmental indicators.

Reptilia.

Reptile remains in the "bone-beds" notably at Aust 2, Westbury Garden Cliff 9, Wetmoor Wood 2, Sedbury Cliff 3, Wainlode Cliff 4, and Watchet Harbour 2 are relatively common, although incomplete. The fossils are dominated by postcranial elements and dental remains from three orders:-

i) Icthyosauria.
ii) Plesiosauria.
iii) Eosuchia.

Unfortunately most of this fossil material is disarticulated and too poorly preserved to be accurately identified. Duffin (1980) and Reynolds (1947) however reviewed (as best they could) the taxonomy of the available plesiosaur and icthyosaur material. There diagnoses are so vague, that in this study only ordinal level identification is used for those two groups.

The third reptilian order was initially described by Owen (1839), on the basis of "spool shaped" vertebrae, as *Rysosteus sp.* but it was not given any detailed taxonomic status. Reynolds (1947) for instance, simply termed it "dinosaurian" while Duffin (1980) thought it was crocodilian.

Von Huene (1934) indepentently described *Rysosteus sp.* as *Pachystropheus sp.* She considered that it was was a thallatosaur and possibly related to the Tertiary Champsosauridae. Comparison of it with the Eocene north American *Champsosaurus sp.* (Erickson 1972) certainly reveals a remarkable similarity between the two forms. The similarities are most striking when comparing the limb and vertebral (both dorsal and caudal) elements. *Rysosteus sp.* is therefore considered to be an Eosuchian.

Erickson (1972) reconstructed *Champsosaurus sp.* as having an aquatic crocodillian habit and *Rysosteus sp.* here is reconstructed in the same manner.

A notable feature of the "bone-bed" is the presence of coprolites, these have been described in detail by Duffin (1981). Some at least are believed to derive from sharks (because of their spiral shape). Generally however it is not possible to ascribe the coprolites to any particular group.

Generally the Westbury Formation vertebrate fauna was dominated by aquatic forms, and was probably marine.

APPENDIX 6. The inflence of other bacterial groups in sediments.

The influence that other bacterial groups (not including:- aerobes sulphate reducers, methanogens and sulphide oxidizers) have on the pore water chemistry has been largely ignored by geomicrobiologists, this is due to the fact that they tend to catalyse reactions that occur anyway, albeit slowly, and their catabolism produces no authigenic minerals. The following section reviews the effect that nitrate reducers, iron and manganese oxidizers and manganese reducers might have on pore water systems.

1) Nitrate Reducers.

The influence of nitrate reducing bacteria has been reviewed by Herbert (1982). Nitrate reducers use nitrate as an electron acceptor and reduce it to nitrite or ammonia, depending if any free oxygen is available as an contributing oxidizing agent. They are both faculative anaerobes and aerobes, and may profoundly influence the pH of the pore water if ammonia is the terminal electron acceptor. Obviously they potentially increase the pore water bicarbonate concentrations as the only reducing agent buried with the sediment is organic matter. Consequently nitrate reduction may cause carbonate precipitation if suitable anions are present.

2) Iron and Manganese Oxidizers.

The influence of iron and manganese oxidizers on pore water chemistry has been discussed by Ghiorse (1984) and Nealson (1983). These organisms utilise oxygen as an oxidizing agent, gain their electrons from the oxidation of reduced iron and manganese species and uptake carbon either heterotrophiclly or autotrophically, generally they live in pH conditions close to neutral. These two groups have little effect on the pore water chemistry in sedimentary systems, except that they might deplete the amount of reduced manganese and iron available for incorporation into calcite cements and thus alter the latters luminescence coefficient.

3) Manganese Reducers.

The influence of manganese reducers has also been largely ignored although they may play a significant role in the production of rhodochrosite (Coleman 1985). Their effect is limited because very little manganese is dissolved in normal seawater (0.2 μg/Kg, Drever 1982).

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